Phase Equilibria and Crystal Structures of Phases in the La–Fe–Ni–O System at 1370 K in Air

E. A. Kiselev^a, N. V. Proskurnina^b, V. I. Voronin^b, and V. A. Cherepanov^a

^a Gorki State University, pr. Lenina 51, Yekaterinburg, 620083 Russia ^b Institute of Metal Physics, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 18, Yekaterinburg, 620219 Russia e-mail: evgenykiselev@e1.ru

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Abstract—The phase equilibria in the La–Fe–Ni–O system have been studied at 1370 K in air, and the La–Fe–Ni–O phase diagram at constant temperature and pressure has been constructed. Based on x-ray diffraction results for samples prepared by standard solid-state reactions and via citrate and nitrate routes, the following solid solutions have been shown to exist at 1370 K in air: LaFe_{1-x}Ni_xO_{3-δ} (0 < $x \le 0.4$, sp. gr. *Pbnm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbnm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. gr. *Pbm*; 0.6 ≤ $x \le 0.4$, sp. *Pb*; 0.6 ≤ $x \le 0.4$, sp. *Pb*; 0.6 ≤ $x \le 0.4$,

0.8, sp. gr. $R\bar{3}c$), La₄(Ni_{1-y}Fe_y)₃O_{10- δ} (0 < y ≤ 0.3), La₃(Ni_{1-z}Fe_z)₂O_{7- δ} (0 < z ≤ 0.05), La₂Ni_{1-v}Fe_vO_{4+ δ} (0 < v ≤ 0.05), Ni_kFe_{3-k}O₄ (0.81 ≤ k ≤ 1.05), Ni_{1-m}Fe_mO (0 < m ≤ 0.05), and Fe_{2-p}Ni_pO₃ (0 < p ≤ 0.04). The lattice constants and structural parameters of single-phase samples have been refined by the Rietveld profile analysis method.

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INTRODUCTION

The study of ABO_{3+ δ} (A = La–Gd and/or alkaline earth; B = Ga, Mn, Cr, Co, Ni, Fe) perovskite and perovskite-related oxides is of great practical interest. Owing to their unique physical and chemical properties, these oxides are being used increasingly as electrode materials for solid oxide fuel cells (SOFCs) [1-4], cathode materials for CO_2 lasers [5], oxidation catalysts [6], and oxygen ion/electron conducting membranes for methane conversion [7, 8]. Practical application of these materials still depends not only on knowledge of their physical properties and electrochemical performance but also on optimization of preparation conditions and knowledge of the thermodynamic stability of all intermediate and final phases as a function of temperature, oxygen partial pressure, and chemical composition of the material.

The pseudobinary system La_2O_3 -Fe₂O₃ in air contains a phase of composition $LaFeO_{3\pm\delta}$, with an orthorhombically distorted perovskite structure (sp. gr. no. 62, *Pbnm* [9, 10] or *Pnma* [4, 11, 12]). In the temperature range 1650–1690 K, the system contains the $LaFe_{12}O_{19}$ oxide, which was reported to have the magnetoplumbite (PbFe₁₂O₁₉) [13] or β -Al₂O₃ [14] structure. The lanthanum ferrite of composition LaFeO_{3±δ} is stable in air up to its melting point, ~2170 K [13, 15].

The ternary system La–Ni–O in air is known to contain $La_{n+1}Ni_nO_{3n+1}$ Ruddlesden–Popper phases, namely, $LaNiO_{3-\delta}$, stable to 1250 K [16] and having a rhombohedrally distorted perovskite structure (sp. gr. $R\bar{3}c$) [9, 12]; La₂NiO_{4+ δ}, stable up to its melting point $(\approx 1970 \text{ K})$ [17] and having a tetragonal structure of the K_2NiF_4 type (sp. gr. *I*4/*mmm*) [17–20]; and the orthorhombic phases La₃Ni₂O_{7- δ} (sp. gr. *Cmcm*) [19, 21–23] and $La_4Ni_3O_{10-\delta}$ (sp. gr. *Cmca*) [19, 22–25]. Zinkevich and Aldinger [26] systematized the available information about the phase equilibria in the La-Ni-O system and evaluated some of the thermodynamic functions of LaNiO_{3- δ}, La₄Ni₃O_{10- δ}, La₃Ni₂O_{7- δ}, and La₂NiO_{4+ δ} using experimental data. According to the phase-diagram data reported by Zinkevich and Aldinger [26] for the La-Ni-O system, $La_4Ni_3O_{10-\delta}$ and $La_3Ni_2O_{7-\delta}$ decompose in air near 1450 and 1500 K, respectively. Thus, the thermodynamic stability of the $La_{n+1}Ni_nO_{3n+1}$ Ruddlesden–Popper phases in air decreases with increasing n and temperature.

The phase relations and crystal structure of LaFe_{1-x}Ni_xO_{3-δ} solid solutions were studied by several groups [4, 12, 27]. Two LaFe_{1-x}Ni_xO_{3-δ} solid-solution phases were found to form in air at 1520 K: one based on the orthorhombic phase LaFeO_{3±δ} (0 < $x \le 0.5$), and the other based on the rhombohedral phase LaNiO_{3-δ} (x = 0.6) [4]. In the composition range $0.7 \le x \le 0.8$, the samples contained, in addition to the rhombohedrally distorted perovskite phase LaFe_{1-x}Ni_xO_{3-δ}, the orthorhombic phase La₄Ni₃O_{10-δ} [4]. The samples with x > 0.8 were found to consist of two phases: La₄Ni₃O_{10-δ} and La₂NiO_{4+δ} [4]. At higher annealing temperatures, 1720–1780 K, Kharton et al. [27] obtained samples with x = 0.4 and 0.5 based on the lan-

thanum ferrite LaFeO_{3±δ}. The mixed oxides LaFe_{0.8}Ni_{0.2}O_{3-δ} and LaFe_{0.7}Ni_{0.3}O_{3-δ} had cubic and rhombohedral structures, respectively [27]. The LaFe_{1-x}Ni_xO_{3-δ} samples prepared by Falcon et al. [12] via a citrate route with a final annealing temperature of 1170 K were single-phase in the ranges $0 \le x \le 0.4$ (sp. gr. *Pnma*) and $x \ge 0.6$ (sp. gr. $R\bar{3}c$). The LaNi_{0.5}Fe_{0.5}O₃ sample consisted of orthorhombic and rhombohedral phases [12].

Kharton et al. [28] prepared La₂Ni_{1-x}Fe_xO_{4+δ} (x = 0.02, 0.1) solid solutions with the K₂NiF₄ structure via a nitrate route in air at temperatures from 1420 to 1890 K, followed by slow cooling to room temperature. The tetragonal cell parameters of La₂Ni_{0.98}Fe_{0.02}O_{4+δ} were a = 3.864 Å and c = 12.661 Å, and those of La₂Ni_{0.9}Fe_{0.1}O_{4+δ} were a = 3.872 Å and c = 12.673 Å [28].

The Fe–Ni–O system in air contains NiFe₂O₄-based spinel solid solutions [29] and NiO-based rock-salt solid solutions. At 1270 K in air, the spinel solid solutions exist in a very narrow composition range [29]. With increasing temperature, the solid-solution range of Ni_xFe_{3-x}O₄ shifts toward the hematite (Fe₂O₃) region and is limited on the Fe-rich side by an Fe : Ni atomic ratio of 2.297 ($x \approx 0.91$) at 1370 K, 2.616 ($x \approx 0.83$) at 1470 K, and 4.969 ($x \approx 0.50$) at 1570 K. NiO does not dissolve in NiFe₂O₄ under any conditions. At 1570 K, the Ni-rich phase boundary of the spinel solid solutions is at Fe : Ni = 2.192, which corresponds to the formula Ni_{0.94}Fe_{2.06}O₄ [29].

Thus, the available information about the phase relations and crystal structures of phases in the La–Fe–Ni–O system is still limited and somewhat contradictory, so that a more in-depth study of this system is needed. The objective of this work was to systematically investigate the phase equilibria in the La–Fe–Ni–O system at 1370 K in air and to refine the structural parameters of the phases involved.

EXPERIMENTAL

Mixed-oxide samples for this investigation were prepared by standard solid-state reactions and via nitrate and citrate routes. The starting reagents used were LaO-D La₂O₃, Fe₂O₃, extrapure-grade NiO, extrapure-grade Fe metal, and Ni metal prepared by reducing nickel oxide at 870 K in flowing hydrogen. To remove adsorbed moisture and gases, the starting reagents were calcined for 2–3 h: La₂O₃ at 1470 K, NiO at 970 K, and Fe₂O₃ at 820 K.

Solid-state reactions were conducted in three steps, by firing the samples at 1120 K for 20 h (I), then at 1220 K for 20 h (II), and finally at 1370 K for 300 h (III). Every 20 h of heat treatment, the samples were quenched to room temperature and reground in an agate mortar with ethanol. In the nitrate and citrate processes, appropriate mixtures of lanthanum oxide (La_2O_3), metallic iron, and metallic nickel were dissolved in dilute extrapure-grade nitric acid, HNO₃.

In the nitrate process, the nitrate solutions were then boiled down, and the mixtures were decomposed at temperatures from 470 to 570 K until no gaseous reaction products were released. The resultant dry residue was ground in an agate mortar and decomposed by firing at 1070 K for 24 h. The powders thus obtained were pressed at 5–15 MPa into disk-shaped samples 8 mm in diameter, which were then heat-treated in air at 1370 K for five days.

In the citrate process, an excess of analytical-grade citric acid monohydrate, $C_6H_5O_4(OH)_3 \cdot H_2O$, was added to the nitrate solutions while heating the mixture. The resulting syruplike citrate and citric acid solutions were boiled down and then decomposed in several steps at temperatures from 470 to 1220 K. In the final step, the powders were heat-treated at 1370 K in air for five to ten days with intermediate grindings every 20 h.

The phase composition and crystal structure of the samples were determined by x-ray diffraction (XRD) at room temperature on DRF-4.0 and DRON-UM1 diffractometers (Cu K_{α} radiation, $2\theta = 15^{\circ}-75^{\circ}$). The lattice periods and structural parameters of single-phase samples were refined by the Rietveld profile analysis method with FullProf 2004.

RESULTS AND DISCUSSION

The phase equilibria in the La–Fe–Ni–O system were studied at 1370 K in air. According to our XRD data for samples quenched from 1370 K to room temperature, the following solid solutions exist in the La–Fe–Ni–O system at $p_{O_2} = 0.21 \times 10^5$ Pa: LaFe_{1-x}Ni_xO_{3- δ} based on lanthanum orthoferrite (LaFeO_{3± δ}) and lanthanum nickelate (LaNiO_{3- δ}, nonexistent under the conditions of this study), La₄(Ni_{1-y}Fe_y)₃O_{10- δ}, La₃(Ni_{1-z}Fe_z)₂O_{7- δ}, La₂Ni_{1-v}Fe_vO_{4+ δ}, Ni_kFe_{3-k}O₄, Ni_{1-m}Fe_mO, and Fe_{2-p}Ni_pO₃.

LaFe_{1-x}Ni_xO_{3- δ} solid solutions. To determine the limits of the LaFe_{1-x}Ni_xO_{3- δ} solid solutions at *T* = 1370 K and *p*_{O2} = 0.21 × 10⁵ Pa, appropriate samples with *x* varied from 0 to 0.9 in steps of 0.05 were prepared by the citrate route. According to XRD data for quenched samples, the LaFe_{1-x}Ni_xO_{3- δ} solid solutions exist in the composition ranges 0 < *x* ≤ 0.4 and 0.6 ≤ *x* ≤ 0.8.

In the range $0 < x \le 0.4$, the solid solutions are isostructural with LaFeO_{3±δ} (sp. gr. *Pbnm*) (Fig. 1). The XRD patterns of the single-phase samples with $0.6 \le x \le 0.8$ could be indexed in rhombohedral symmetry (sp. gr. $R\bar{3}c$) (Fig. 2). Tables 1 and 2 list the structural



Fig. 1. Rietveld refinement profile for LaFe_{0.6}Ni_{0.4}O_{3 - δ}: the open circles represent the raw XRD data, the upper continuous line is the calculated profile, and the lower continuous line is the difference plot.



Fig. 2. Rietveld refinement profile for LaFe_{0.4}Ni_{0.6}O_{3 – δ}: the open circles represent the raw XRD data, the upper continuous line is the calculated profile, and the lower continuous line is the difference plot.

x		0.4	0.35	0.3	0.2	0.15	0.1	0.05	0
<i>a</i> , Å		5.523(2)	5.526(4)	5.531(5)	5.540(7)	5.549(7)	5.549(7)	5.549(7)	5.551(6)
<i>b</i> , Å		5.486(2)	5.495(4)	5.503(5)	5.521(7)	5.512(7)	5.536(7)	5.542(7)	5.561(5)
<i>c</i> , Å		7.774(4)	7.786(8)	7.795(8)	7.815(1)	7.849(1)	7.832(1)	7.853(1)	7.846(9)
X	O(1)	0.064(4)	0.045(7)	0.073(9)	0.07(2)	0.06(1)	0.114(7)	0.06(2)	0.07(2)
Y		0.496(2)	0.494(6)	0.506(5)	0.492(8)	0.489(7)	0.480(6)	0.489(7)	0.494(4)
X	O(2)	-0.277(2)	-0.276(6)	-0.265(9)	-0.26 (1)	-0.258(9)	-0.22(1)	-0.25(1)	-0.266(7)
Y		0.263(4)	0.274(6)	0.288(6)	0.26(1)	0.309(6)	0.28(1)	0.26(1)	0.271(7)
Ζ		0.030(2)	0.034(4)	0.024(6)	0.035(9)	0.040(6)	0.005(6)	0.04(1)	0.035(7)
X	La	-0.0028(7)	-0.003(2)	-0.004(1)	-0.000(4)	0.001(4)	-0.005(1)	0.003(4)	-0.001(4)
Y		0.0198(2)	0.0213(5)	0.0218(5)	0.0221(8)	0.0203(7)	0.0257(5)	0.0238(7)	0.0276(4)
$2 \times l(Ni)$	/Fe–O), Å	1.976(4)	1.953(6)	1.99(1)	2.00(2)	1.99(1)	2.06(1)	1.99(3)	2.00(2)
$2 \times l$ (Ni/Fe–O), Å		1.91(2)	1.975(3)	1.88(4)	1.95(8)	2.19(4)	2.22(6)	2.03(6)	2.01(4)
$2 \times l$ (Ni/Fe–O), Å		2.02(2)	2.002	2.06(4)	2.00(8)	1.80(4)	1.70(6)	1.95(6)	1.97(4)

Table 1. Structural parameters of $LaFe_{1-x}Ni_xO_{3-\delta}$ in the range $0 \le x \le 0.4$ (sp. gr. *Pbnm*: La in *X*, *Y*, 0.25; Fe/Ni in 0.5, 0, 0; O(1) in *X*, *Y*, 0.25; O(2) in *X*, *Y*, *Z*)

Table 2. Structural parameters of $LaFe_{1-x}Ni_xO_{3-\delta}$ in the range $0.6 \le x \le 0.8$ (sp. gr. $R\overline{3}c$: La in 0, 0, 0.25; Fe/Ni in 0, 0, 0; O in *X*, 0, 0.25)

x	0.8	0.75	0.7	0.6
<i>a</i> , Å	5.509(4)	5.485(3)	5.492(6)	5.502(2)
<i>c</i> , Å	13.290(1)	13.212(8)	13.222(1)	13.244(6)
X(O)	0.444(2)	0.452(3)	0.449(3)	0.449(2)
$\overline{3 \times l(\text{La-O}), \text{\AA}}$	3.06(1)	3.002(9)	3.02(2)	3.031(9)
$3 \times l$ (La–O), Å	2.45(1)	2.482(4)	2.468(9)	2.470(6)
$3 \times l$ (La–O), Å	2.744(6)	2.724(5)	2.729(8)	2.734(4)
$6 \times l$ (Ni/Fe–O), Å	1.962(7)	1.946(6)	1.950(5)	1.954(4)

parameters extracted from our XRD data for the LaFe_{1-x}Ni_xO_{3- δ} solid solutions with 0 < x ≤ 0.4 and 0.6 ≤ x ≤ 0.8, respectively, by the Rietveld profile analysis method. The LaFe_{1-x}Ni_xO_{3- δ} samples with x = 0.45 and 0.5 consisted of two perovskite phases. For x > 0.8, the XRD patterns showed reflections from the rhombohedrally distorted perovskite LaFe_{0.2}Ni_{0.8}O_{3- δ}, La₄(Ni_{1-v}Fe_v)₃O_{10- δ}, and NiO.

For the convenience of comparison, the unit-cell parameters of the orthorhombic (*O*) and rhombohedral (*R*) structures were reduced to a cubic (*C*) cell using the relations $a_C = a_0/\sqrt{2}$, $b_C = b_0/\sqrt{2}$, $c_C = c_0/2$, and $a_C = a_R/\sqrt{2}$ in the composition range $0 \le x \le 0.8$ (Fig. 3). As

seen in Fig. 3, the lattice parameters decrease systematically with increasing *x*, which can be accounted for by the size factor: the ionic radius of Fe³⁺ (r = 0.645 Å at CN = 6) is larger than that of Ni³⁺ (r = 0.56 Å at CN = 6) [30].

Our results on the extent of the $LaFe_{1-x}Ni_xO_{3-\delta}$ solid solutions in the pseudobinary system $LaFeO_3$ -LaNiO₃ are, on the whole, in reasonable agreement with earlier data [4, 12].

In air, lanthanum nickelate, LaNiO_{3- δ}, is stable up to 1250 K. At higher temperatures, its reduction leads to the formation of phases containing nickel in oxidation states below 3+ [16, 26]. Partial replacement of Ni by Fe, which is typically in a higher oxidation state than



Fig. 3. Symmetry and pseudocubic cell parameters of $LaFe_{1-x}Ni_xO_{3-\delta}$ solid solutions.

is Ni, all other factors being the same, raises the temperature stability limit of the rhombohedrally distorted perovskite phase. The extents of the nickel-rich LaFe_{1-x}Ni_xO_{3- δ} solid solutions determined in this study at 1370 K and by Chiba et al. [4] at 1520 K are consistent with the decomposition temperature of LaNiO_{3- δ} (1250 K) [16], which allows us to evaluate the composition stability limit of the rhombohedral solid solutions in air as a function of temperature (Fig. 4).

La₄(Ni_{1-y}Fe_y)₃O_{10- δ} solid solutions. To ascertain whether La₄(Ni_{1-y}Fe_y)₃O_{10- δ} solid solutions exist at 1370 K in air, we prepared samples with y = 0, 0.05, 0.1, 0.15, 0.2, 0.3, and 0.4.

XRD examination showed that the samples with $0 \le y \le 0.3$ were single-phase. The XRD pattern of $La_4Ni_{1.8}Fe_{1.2}O_{10-\delta}$ showed additional reflections from $La_2Ni_{1-\nu}Fe_{\nu}O_{4+\delta}$ and $LaFe_{1-x}Ni_xO_{3-\delta}$. The $La_4(Ni_{1-\nu}Fe_{\nu})_3O_{10-\delta}$ solid solutions had an orthorhombic structure (sp. gr. *Cmca*). The Rietveld-refined lat-



Fig. 4. Stability of rhombohedral $LaFe_{1-x}Ni_xO_{3-\delta}$ solid solutions in air.

tice parameters of these solid solutions are listed in Table 3.

La₃(Ni_{1-z}Fe_z)₂O_{7- δ} solid solutions. To determine the extent and structure of La₃(Ni_{1-z}Fe_z)₂O_{7- δ} solid solutions at 1370 K in air, we prepared samples with z varied from 0 to 0.2 in steps of 0.05.

The XRD patterns of all the samples prepared by standard solid-state reactions at 1370 K in 100 h indicated that the system did not reach equilibrium: in addition to the major phase, the samples contained $La_2Ni_{1-v}Fe_vO_{4+\delta}$, $La_4(Ni_{1-v}Fe_v)_3O_{10-\delta}$, and NiO, whereas, according to the Gibbs phase rule, the maximum number of phases in equilibrium is three. Using the nitrate and/or citrate routes, we obtained single-phase samples with z = 0 and 0.05 by firing at 1370 K in air for 100 h. The samples with z = 0.1, 0.15, and 0.2 contained $La_2Ni_{1-v}Fe_vO_{4+\delta}$ and $La_4(Ni_{1-v}Fe_v)_3O_{10-\delta}$.

The XRD data for the single-phase samples were analyzed by the Rietveld method. The La₃(Ni_{1-z}Fe_z)₂O_{7- δ} solid solutions (0 < z \leq 0.05) have

у	<i>a</i> , Å	$b, \mathrm{\AA}$	<i>c</i> , Å	<i>V</i> , Å ³	R _{Br}	R_{f}
0	5.413(1)	28.007(1)	5.463(1)	828.32(1)	3.51	2.81
0.05	5.413(1)	27.983(0)	5.466(1)	827.85(1)	2.99	2.15
0.1	5.423(2)	28.018(1)	5.479(1)	832.54(1)	3.65	3.07
0.15	5.430(1)	28.038(6)	5.491(0)	836.03(2)	1.61	1.40
0.2	5.438(7)	28.073(6)	5.497(1)	839.16(3)	1.69	1.53
0.3	5.452(4)	28.024(8)	5.569(3)	850.97(2)	3.27	2.84

Table 3. Lattice parameters of $La_4(Ni_{1-y}Fe_y)_3O_{10-\delta}$ ($0 \le y \le 0.3$)

Z.	<i>a</i> , Å	b, Å	<i>c</i> , Å	<i>V</i> , Å ³	R _{Br}	R_{f}
0	5.4495(1)	20.5350(1)	5.3959(1)	603.83(1)	2.93	1.51
0.05	5.4578(1)	20.4854(1)	5.4053(1)	604.34(1)	2.17	1.91

Table 4. Lattice parameters of $La_3(Ni_{1-z}Fe_z)_2O_{7-\delta}$

an orthorhombic structure (sp. gr. *Cmcm*). Their refined unit-cell parameters and volume are listed in Table 4.

La₂Ni_{1-v}Fe_vO_{4+ δ} solid solutions. Earlier, the La₂Ni_{1-v}Fe_vO_{4+ δ} solid solutions with v = 0.02 and 0.1 were prepared by Kharton et al. [28] via a nitrate route in air at temperatures from 1420 to 1890 K. To verify their results and determine the La₂Ni_{1-v}Fe_vO_{4+ δ} solidsolution range at 1370 K in air, we prepared samples with v = 0, 0.05, 0.1, 0.15, and 0.2 by the nitrate process.

According to our XRD data, the $La_2Ni_{1-v}Fe_vO_{4+\delta}$ solid-solution series at 1370 K in air is limited by v = 0.05. Starting at v = 0.1, all of the samples were threephase, independent of the preparation procedure: their XRD patterns showed reflections from the $La_2Ni_{0.95}Fe_{0.05}O_{4+\delta}$ solid solution, La_2O_3 , and $La_4Ni_{2.1}Fe_{0.9}O_{10-\delta}$. The single-phase samples had a tetragonal structure of the K₂NiF₄ type (sp. gr. *14/mmm*). Table 5 lists the refined lattice parameters of the $La_2Ni_{1-v}Fe_vO_{4+\delta}$ solid solutions and the atomic positional parameters and bond lengths in their structure. The lattice parameters obtained in this study agree well with those reported by Kharton et al. [28].

Ni_kFe_{3-k}O₄ solid solutions. To evaluate the extent of this solid-solution series, we prepared samples with k = 0.75, 0.9, 0.96, 1.0, 1.08, 1.2, 1.35, and 1.5 by standard solid-state reactions. Our XRD data for samples air-quenched from 1370 K indicate that the Ni_kFe_{3-k}O₄ spinel solid solutions (sp. gr. *Fd3m*) exist in the composition range $0.81 \le k \le 1.05$. According to Paladino [29], at 1370 K this solid-solution series is limited on the Fe-rich side by k = 0.91, and the Ni_kFe_{3-k}O₄ spinel dissolves no NiO, that is, $k \le 1$.

The Ni-rich phase boundary of Ni_kFe_{3-k}O₄ lies between k = 1.0 and k = 1.08, and the Fe-rich boundary lies in the range 0.75 < $k \le 0.9$. In determining the stoichiometry range of the spinel solid solutions, we evaluated the percentages of the coexisting phases in twophase samples using FullProf 2004. According to least squares fitting results, the spinel solid solutions exist in the composition range $0.81 \le k \le 1.05$. Table 6 lists the refined unit-cell parameters and volume of these solid solutions and the atomic position coordinates in their structure.

 $Ni_{1-m}Fe_mO$ and $Fe_{2-p}Ni_pO_3$ solid solutions. To evaluate the extent of the $Ni_{1-m}Fe_mO$ solid-solution series at 1370 K in air, we prepared samples with m = 0.02, 0.05, and 0.1 by standard solid-state reactions.

XRD examination showed that the Ni_{0.98}Fe_{0.02}O and Ni_{0.95}Fe_{0.05}O samples were single-phase and had the NiO structure (sp. gr. $Fm\bar{3}m$). Their lattice parameters are indicated in Table 7.

Thus, the limit of the Ni_{1-m}Fe_mO solid solution lies in the range $0.05 \le m < 0.1$. The extent of this solid solution was not refined further in this study, and, in analyzing phase equilibria, we took, as a first approximation, that its limit is at $m \simeq 0.075$.

From our XRD data for $Fe_{2-p}Ni_pO_3$ samples with p = 0.04 and 0.1, it follows that the nickel solubility in hematite is approximately 2 mol % (p = 0.04).

Phase diagram of the La–Fe–Ni–O system. The phase relations in this system cannot be adequately represented on a plane using the oxides in equilibrium under the conditions of interest as the constituent components, because the constituent oxides and intermediate phases may differ in the oxidation state of the 3*d* transition metals. Representation of the phase diagram of a quaternary system in the form of a tetrahedron is inconvenient in practice.

A more convenient approach for visualizing the phase equilibria in the La–Fe–Ni–O system is to project

Table 5. Structural parameters of $La_2Ni_{1-v}Fe_vO_{4+\delta}$ (sp. gr. *I4/mmm*: La in 0, 0, *Z*; Ni(Fe) in 0, 0, 0; O(1) in 0, 0.5, 0; O(2) in 0, 0, *Z*)

V	0	0.05
<i>a</i> , Å	3.8616(1)	3.8665(2)
<i>c</i> , Å	12.6672(1)	12.6674(1)
Z(La)	0.3612(0)	0.3670(0)
Z (O(2))	0.1753(3)	0.1723(1)
<i>V</i> , Å ³	188.89(3)	189.37(4)
$\overline{4 \times l(\text{Ni-O}(1))}, \text{\AA}$	1.931(2)	1.933(1)
$\overline{2 \times l(\text{Ni-O}(2)), \text{\AA}}$	2.221(4)	2.183(0)
$\overline{4 \times l(\text{La-O}(1))}$, Å	2.611(1)	2.564(1)
$\overline{4 \times l(\text{La-O}(2))}, \text{\AA}$	2.769(2)	2.779(3)
<i>l</i> (La–O(2)), Å	2.355(1)	2.466(2)
R _{Br}	3.86	2.60
$\overline{R_f}$	4.28	3.42



Fig. 5. 1370-K isotherm of the La-Fe-Ni-O system in air.

the phase equilibria onto the plane of metallic components. Thus, in the triangle we use, compositions are expressed as the mole fractions of the metallic components, and the oxygen content is assumed to be equal to its equilibrium value.

Based on our XRD data for samples prepared at 1370 K and $p_{O_2} = 0.21 \times 10^5$ Pa, we identified 18 phase

fields in the phase diagram of the pseudoternary system La_2O_3 -Fe₂O₃-NiO (Fig. 5). The points in the phase diagram represent the compositions studied. The phase fields are listed in Table 8.

The equilibrium compositions $La_4Ni_{2.7}Fe_{0.3}O_{10-\delta}$ and $LaFe_{0.95}Ni_{0.05}O_{3-\delta}$ in the three-phase regions *XI* and *XV* were determined from the refined lattice param-

k	X = Y = Z	a = b = c, Å	<i>V</i> , Å ³	R_{f}	R _{Br}
0.9	0.2518(7)	8.333(5)	578.73(7)	3.22	1.93
0.96	0.2516(7)	8.339(6)	579.88(7)	1.5	1.12
1.0	0.2529(6)	8.334(4)	578.93(6)	0.74	0.51

Table 6. Lattice parameters of Ni_kFe_{3-k}O₄ solid solutions (sp. gr. *Fd3m*: Ni in 0.125, 0.125, 0.125; Fe in 0.5, 0.5, 0.5; O in *X*, *Y*, *Z*)

Table 7. Lattice parameters of $Ni_{1-m}Fe_mO$ solid solutions (sp. gr. Fm3m: Ni/Fe in 0, 0, 0; O in 0.5, 0.5, 0.5)

Composition	a = b = c, Å	<i>V</i> , Å ³	R_{f}	R _{Br}
Ni _{0.98} Fe _{0.02} O	4.1753(5)	72.79(1)	0.30	0.16
Ni _{0.95} Fe _{0.05} O	4.1752(4)	72.78(1)	0.46	0.28

Field	Phase composition
I	$La_2O_3, LaFe_{1-x}Ni_xO_{3-\delta} \ (0 \le x \le 0.4)$
II	La_2O_3 , $LaFe_{0.6}Ni_{0.4}O_{3-\delta}$, $LaFe_{0.4}Ni_{0.6}O_{3-\delta}$
III	La_2O_3 , $LaFe_{0.4}Ni_{0.6}O_{3-\delta}$, $La_4Ni_{2.1}Fe_{0.9}O_{10-\delta}$
IV	La_2O_3 , $La_2Ni_{0.95}Fe_{0.05}O_{4+\delta}$, $La_4Ni_{2.1}Fe_{0.9}O_{10-\delta}$
V	$La_2O_3, La_2Ni_{1-v}Fe_vO_{4+\delta} \ (0 \le v \le 0.05)$
VI	$La_{2}Ni_{0.95}Fe_{0.05}O_{4+\delta}, La_{4}Ni_{2.1}Fe_{0.9}O_{10-\delta}, La_{3}Ni_{1.9}Fe_{0.1}O_{7-\delta}$
VII	$La_2Ni_{1-v}Fe_vO_{4+\delta}$ (0 ≤ v ≤ 0.05), $La_3(Ni_{1-z}Fe_z)_2O_{7-\delta}$ (0 ≤ z ≤ 0.05)
VIII	$La_3(Ni_{1-z}Fe_z)_2O_{7-\delta} (0 \le z \le 0.05), La_4(Ni_{1-y}Fe_y)_3O_{10-\delta} (0 \le y \le 0.3)$
IX	LaFe _{1-x} Ni _x O _{3-δ} (0.55 \leq x \leq 0.8), La ₄ (Ni _{1-y} Fe _y) ₃ O _{10-δ} (0.1 \leq y \leq 0.3)
X	NiO, $La_4(Ni_{1-y}Fe_y)_3O_{10-\delta}$ ($0 \le y \le 0.1$)
XI	$La_4Ni_{2.7}Fe_{0.3}O_{10-\delta}, LaFe_{0.2}Ni_{0.8}O_{3-\delta}, NiO$
XII	LaFe _{1-x} Ni _x O _{3-δ} (0.6 ≤ x ≤ 0.8), Ni _{1-m} Fe _m O (0 ≤ m ≤ 0.075)
XIII	$Ni_{0.925}Fe_{0.075}O$, $LaFe_{0.4}Ni_{0.6}O_{3-\delta}$, $LaFe_{0.6}Ni_{0.4}O_{3-\delta}$
XIV	LaFe _{1-x} Ni _x O _{3-δ} (0.05 \leq x \leq 0.4), Ni _{0.925} Fe _{0.075} O
XV	$Ni_{0.925}Fe_{0.075}O$, $LaFe_{0.95}Ni_{0.05}O_{3-\delta}$, $Ni_{1.05}Fe_{1.95}O_4$
XVI	LaFe _{1-x} Ni _x O _{3-δ} (0 ≤ x ≤ 0.05), Ni _k Fe _{3-k} O ₄ (0.81 ≤ k ≤ 1.05)
XVII	$LaFeO_{3+\delta}, Fe_{1.96}Ni_{0.04}O_3, Ni_{0.81}Fe_{2.19}O_4$
XVIII	LaFe _{1-x} Ni _i O _{3-δ} (0 ≤ x ≤ 0.05), Fe _{2-p} Ni _p O ₃ (0 ≤ p ≤ 0.04)

Table 8. Phase fields in the La–Fe–Ni–O system at 1370 K and $p_{O_2} = 0.21 \times 10^5$ Pa

eters of three-phase samples and the known composition dependences of lattice parameters for the $La_4(Ni_{1-y}Fe_y)_3O_{10-\delta}$ and $LaFe_{1-x}Ni_xO_{3-\delta}$ solid-solution series.

CONCLUSIONS

The phase equilibria in the La–Fe–Ni–O system at 1370 K in air were studied by XRD using samples prepared via nitrate and citrate routes and by standard solid-state reactions, and the La–Fe–Ni–O phase diagram at constant temperature and pressure was constructed. The lattice constants and some structural parameters of the solid solutions in this system were refined by the Rietveld profile analysis method.

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