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Phase Equilibria and Structure of Solid Solutions in the La–Co–Fe–O System at 1100°C

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Abstract—Phase equilibria in the La–Co–Fe–O system are studied at 1100°C in air using samples prepared by the citrate, nitrate, and conventional ceramic routes. The stability regions and structures of solid solutions in the La–Co–Fe–O system are determined by x-ray powder diffraction: $LaCo_{1-y}Fe_yO_{3-\delta}$ ($0 < y \le 0.25$, sp. gr. $R\bar{3}c$; $0.775 \le y < 1$, sp. gr. $Pbnm$), $Co_{1-y}Fe_yO$ ($0 < y \le 0.13$, NaCl-type structure, sp. gr. $Fm3m$), and $Fe_{3-x}Co_xO_4$ ($0.84 \le x \le 1.38$, sp. gr. $Fd3m$). The structural parameters of phase-pure solid solutions are determined by the Rietveld method. The composition dependences of lattice parameters are presented for $LaCo_{1-y}Fe_yO_{3-\delta}$ ($0 < y \le 0.25$) and $Fe_{3-x}Co_xO_4$ ($0.84 \le x \le 1.38$). The 1100°C isotherm of the pseudoternary system La_2O_3–CoO–Fe_2O_3 in air is constructed.

INTRODUCTION

ABO_3 perovskite oxides with A = rare-earth and/or alkaline-earth metals and B = Mn, Cr, Co, Ni, and Fe have been recently the subject of intense attention owing to their high catalytic activity and good electrical and magnetic properties [1–4]. Of particular interest is the use of Sr-, Ca-, and Ni-substituted cobaltites and ferrites in fabricating gas-tight oxygen-ion-conducting ceramic membranes for methane conversion applications [4, 5]. The broad application field of the materials in question is due to the high stability of the perovskite structure, which offers the possibility of widely varying their oxygen stoichiometry and performing extensive A- and/or B-site doping with no significant structural changes. However, little or no data have been reported on the phase equilibria in oxide systems containing rare-earth and 3*d* transition metals.

In this paper, we report our findings on the stability regions and structures of solid solutions in the La–Co–Fe–O system at 1100°C in air.

EXPERIMENTAL

Samples for this investigation were synthesized by standard solid-state reactions and by the nitrate and citrate routes. Before synthesis, the starting reagents (99.99+%-pure La_2O_3, extrapure-grade Co_3O_4 and Fe_2O_3, and metallic cobalt and iron) were calcined in air for 3–4 h to remove adsorbed gases and moisture: La_2O_3 at 1200°C, Co_3O_4 at 750°C, and Fe_2O_3 at 500°C. Cobalt and iron metals were obtained by reducing the corresponding oxides at 600°C in flowing hydrogen. Solid-state reactions were conducted in air at temperatures from 850 to 1100°C with several intermediate grindings. The annealing time in the last step was 80–400 h.

In the nitrate and citrate processes, the starting reagents were dissolved in a small excess of dilute nitric acid. Next, two procedures were used. In one of them, to the resultant solution was added crystalline citric acid hydrate powder, and the solution was boiled down. The dry residue was slowly heated from 300 to 800°C with several isothermal holds. In the final step, the sample was fired at 1100°C in air for 80–120 h. In the other procedure, the nitrate mixture was melted and decomposed at 200–300°C with vigorous stirring until no gaseous reaction products were released. The resultant mixture was ground in an agate mortar and decomposed by firing at 800°C for 10 h. The powder thus obtained was pressed at 5–10 MPa into disk-shaped samples 8 mm in diameter, which were then heat-treated at 1100°C for 24 h.

In the three procedures, the samples were cooled to room temperature at a rate of 300°C/min. X-ray diffraction (XRD) studies were carried out on DRF-4.0 (phase analysis) and DRON-UM1 (structural analysis) diffractometers (CuK_α radiation, $2\theta = 10°–75°$). In structure determination and refinement of lattice parameters, we used the Rietveld profile analysis method.

RESULTS AND DISCUSSION

The phase equilibria and crystal structure of solid solutions in the La–Co–Fe–O system were studied at 1100°C, using 90 samples prepared as described above.

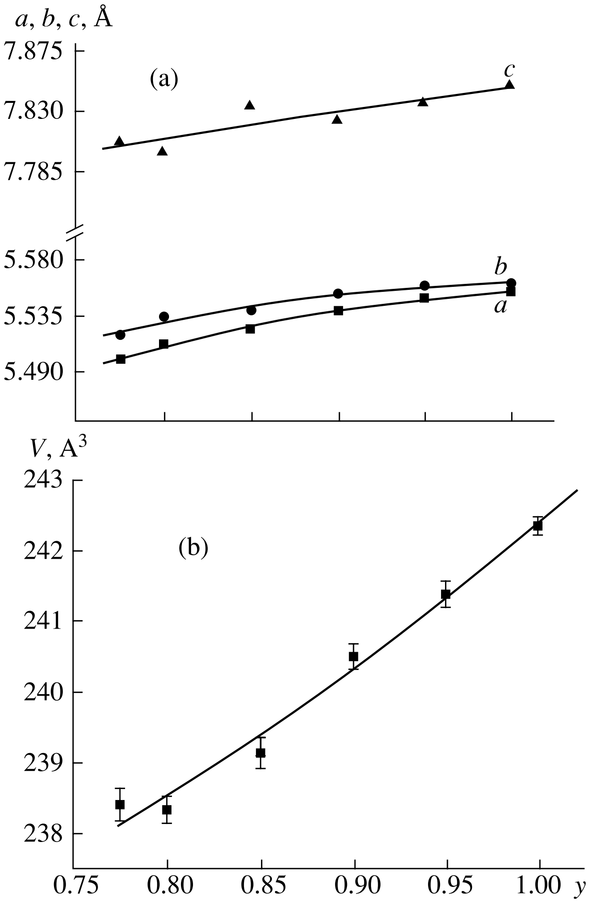

Fig. 1. (a) Unit-cell parameters and (b) volume as functions of Fe content for $LaCo_{1-y}Fe_yO_3$ ($0.775 \le y < 1$) solid solutions.

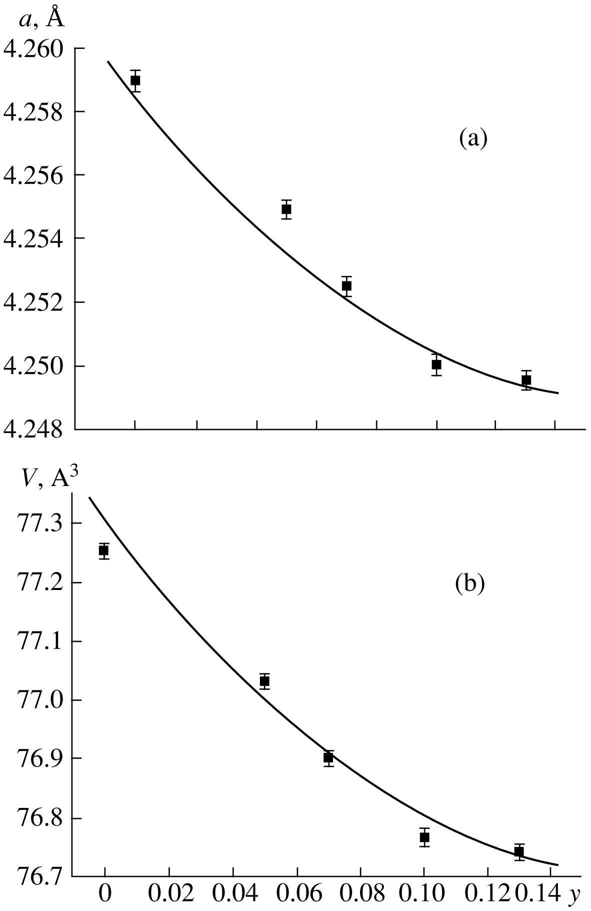

Fig. 2. (a) Unit-cell parameter and (b) volume as functions of Fe content for $Co_{1-y}Fe_yO$ ($0 < y \le 0.13$) solid solutions.

$LaCo_{1-y}Fe_yO_{3-\delta}$ solid solutions. Earlier, $LaCo_{1-y}Fe_yO_{3-\delta}$ solid solutions were prepared by Rao *et al.* [2] and Sagdahl *et al.* [3], but detailed data on the synthesis and structure of these solid solutions are not available in the literature.

To ascertain whether $LaCo_{1-y}Fe_yO_{3-\delta}$ solid solutions exist at 1100°C in air, we prepared samples with $0 < y \le 1.0$ at 0.05 intervals. As shown by XRD examination of quenched samples, $LaCo_{1-y}Fe_yO_{3-\delta}$ solid solutions exist in the composition ranges $0 < y \le 0.25$

Table 1. Structural parameters of $LaCo_{1-y}Fe_yO_3$ ($0.0 \le y \le 0.25$) samples air-quenched from 1000°C (sp. gr. $R\bar{3}c$: La in (0 0 0.25), Co(Fe) in (0 0 0), O in (X 0 0.25))

y		0	0.05	0.1	0.15	0.2	0.25
X		0.4765(4)	0.4379(3)	0.4434(3)	0.4525(3)	0.4490(4)	0.4508(2)
l (La–O), Å	×3	2.8454	3.0581	3.0312	2.9823	3.0029	2.9964
	×3	2.5900	2.3820	2.4145	2.4644	2.4468	2.4592
	×6	2.6888	2.7098	2.7088	2.7051	2.7078	2.7108
l (La–Co), Å	×2	3.2697	3.2734	3.2765	3.2788	3.2795	3.2849
	×6	3.3220	3.3250	3.3284	3.3292	3.3309	3.3347
l (Co–O), Å	×6	1.9147	1.9419	1.9389	1.9323	1.9358	1.9369
V, Å³		335.4(0)	335.7(1)	335.9(2)	336.9(2)	337.4(1)	338.7(1)
a, Å		5.435(1)	5.440(0)	5.446(0)	5.447(0)	5.450(1)	5.456(0)
c, Å		13.079(3)	13.094(1)	13.106(1)	13.115(1)	13.118(1)	13.140(1)

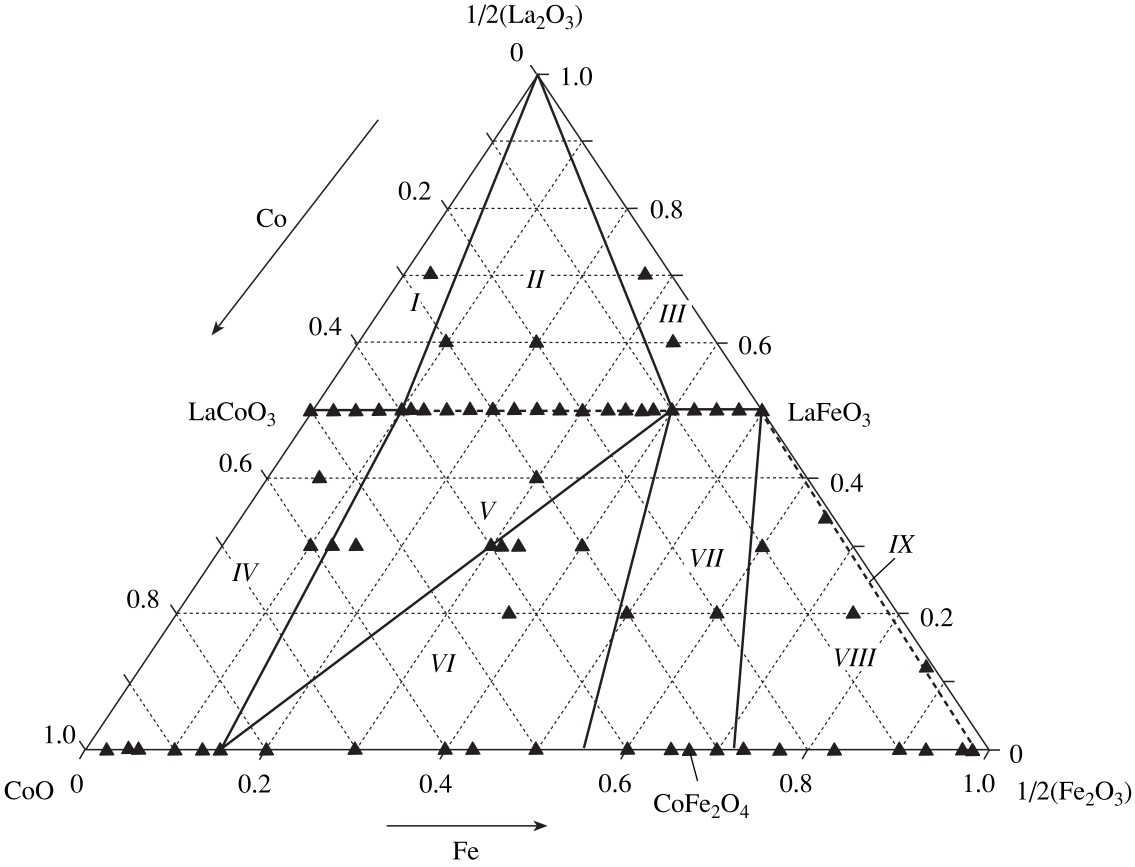

Fig. 3. 1100°C isotherm of the pseudoternary system La_2O_3–CoO–Fe_2O_3 at $p_{O_2} = 0.21 \times 10^5$ Pa; (*I*–*IX*) see Table 3.

and $0.775 \le y < 1$. The use of starting mixtures prepared by the nitrate or citrate route reduced the synthesis time from 240 to 70 h.

The XRD patterns of phase-pure solid solutions with $0 < y \le 0.25$ could be indexed in a rhombohedral unit cell (sp. gr. $R\bar{3}c$). The unit-cell parameters of these solid solutions and the positional parameters and bond distances in their structure are listed in Table 1. With increasing Fe content, the unit-cell parameters and volume increase steadily, in line with the larger ionic radius of Fe^{3+} ($r = 0.645$ Å for CN = 6) compared to that of Co^{3+}($r = 0.61$ Å for CN = 6) [6].

Solid solutions with $0.775 \le y < 1$ crystallize in the $LaFeO_3$ structure (orthorhombic symmetry, sp. gr. *Pbnm*). Their unit-cell parameters as functions of Fe content are shown in Fig. 1.

The samples with $0.25 < y < 0.775$ consisted of a mixture of the $R\bar{3}c$ and *Pbnm* terminal solid solutions.

Phase equilibria in the Co–Fe–O system. Under the conditions typically used to study phase equilibria in 3*d* transition metal–oxygen systems, the equilibrium

Table 2. Structural parameters of $Fe_{3-x}Co_xO_4$ solid solutions (sp. gr. *Fd*3*m*: Fe in (0.125 0.125 0.125), Co(1) in (0.5 0.5 0.5), Co(2) in (0 0 0), O(1) in (*X Y Z*))

x	0.9	1.0	1.05	1.2
$X = Y = Z$	0.254(1)	0.261 (2)	0.259 (4)	0.259 (3)
a, Å	8.378(1)	8.386 (1)	8.385 (1)	8.366 (1)
V, Å^3	587.9(1)	589.8 (1)	589.5 (1)	585.5 (1)
R_B	4.29	4.28	5.29	3.25
R_f	3.44	3.48	4.79	3.74

Table 3. Phase fields in the composition triangle of the La–Co–Fe–O system

Phase field in Fig. 3	Phases in equilibrium
I	$LaCo_{1-y}Fe_yO_3$ ($0.0 \le y \le 0.25$)
	La_2O_3
II	$LaCo_{0.75}Fe_{0.25}O_3$
	$LaCo_{0.225}Fe_{0.775}O_3$
	La_2O_3
III	$LaCo_{1-y}Fe_yO_3$ ($0.775 \le y \le 1.0$)
	La_2O_3
IV	$LaCo_{1-y}Fe_yO_3$ ($0.0 \le y \le 0.25$)
	$Co_{1-y}Fe_yO$ ($0.0 \le y \le 0.13$)
V	$LaCo_{0.75}Fe_{0.25}O_3$
	$LaCo_{0.225}Fe_{0.775}O_3$
	$Co_{0.87}Fe_{0.13}O$
VI	$LaCo_{0.225}Fe_{0.775}O_3$
	$Co_{0.87}Fe_{0.13}O$
	$Co_{1.38}Fe_{1.62}O_4$
VII	$LaCo_{1-y}Fe_yO_3$ ($0.775 \le y \le 0.97$)
	$Co_xFe_{3-x}O_4$ ($0.84 \le x \le 1.38$)
VIII	$LaCo_{0.03}Fe_{0.97}O_3$
	$Co_{0.84}Fe_{2.16}O_4$
	$Co_{0.06}Fe_{1.94}O_3$
IX	$LaCo_{1-y}Fe_yO_3$ ($0.97 \le y \le 1.0$)
	$Fe_{2-x}Co_xO_3$ ($0.0 \le x \le 0.03$)

phases in the Co–Fe–O system are CoO (NaCl structure) and hematite, Fe_2O_3. Earlier, this system was reported to contain solid solutions based on these oxides [7–9] and also $Fe_{3-x}Co_xO_4$ spinel solid solutions [1], but these solid solutions have not been studied in sufficient detail, and available data are, to some extent, contradictory.

As shown by XRD examination of quenched samples, hematite-based $Fe_{2-x}Co_xO_3$ solid solutions exist in the composition range $0 < x \le 0.03$. Thus, under the conditions of this study (1100°C, air) the Co_2O_3 solubility in Fe_2O_3 (about 3 mol %) is notably lower than that reported earlier [8, 9].

$Fe_{3-x}Co_xO_4$ solid solutions exist in the range $0.84 \le x \le 1.38$. Both phase boundaries are slightly shifted toward CoO in comparison with earlier results [1]. The unit-cell parameters of single-phase samples are listed in Table 2.

To assess the solubility of iron in cobalt oxide, we prepared $Co_{1-y}Fe_yO$ samples with $y = 0.05$, 0.07, 0.1, 0.13, 0.15, and 0.2. According to XRD data, all of the samples annealed at 1100°C for 120–200 h (except for $y = 0.15$ and 0.2) were single-phase. The XRD patterns of the samples with $y > 0.13$ showed, along with reflections from the major phase CoO, peaks attributable to a spinel structure. The CoO-based solid solutions belong to the *Fm*3*m* space group. It is well known [8] that cobalt oxide in air is a nonstoichiometric, cation-deficient compound, $Co_{1-z}O$, with a disordered arrangement of the Co vacancies. Fe substitution for Co must increase the deviation from stoichiometry, reducing the lattice parameters of the material, as observed in our data (Fig. 2).

La–Co–Fe–O phase diagram. Phase relations in a quaternary system can be represented using a tetrahedron. A more convenient, planar representation can be obtained using the method of sections. This method, however, is inapplicable to the system under consideration because the starting 3*d* metal oxides are in different oxidation states, and their compositions and the compositions of the reaction products do not all lie in the same plane. For this reason, we used projections onto the plane of metallic components, an approach often used to represent such systems. The oxygen content of condensed phases in each point of a projection is assumed to be equal to the thermodynamically equilibrium value and is not indicated in the composition triangle.

Based on XRD data, the composition triangle of the La–Co–Fe–O system at 1100°C and $p_{O_2} = 0.21 \times 10^5$ Pa can be divided into nine phase fields (Fig. 3). The triangles in the phase diagram represent the compositions studied. The designations of the phase fields are explained in Table 3.

CONCLUSIONS

The stability regions and structures of solid solutions in the La–Co–Fe–O system at 1100°C in air are determined.

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