

Phase Equilibria in the La_2O_3 – Ga_2O_3 – CoO System at 1100°C

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Received August 15, 2006; in final form, December 6, 2006

Abstract—The phase equilibria in the La_2O_3 – Ga_2O_3 – CoO system have been studied at 1100°C in air, using samples prepared by a standard ceramic processing technique from oxides and by a glycine–nitrate combustion process. The composition ranges and structures of solid solutions in this system have been determined by x-ray powder diffraction: $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ ($0 < x \leq 0.05$), $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0 < x \leq 0.10$), $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ ($0 < x \leq 0.20$), $\text{Co}_{1-x}\text{Ga}_{2+x}\text{O}_4$ ($-0.20 \leq x \leq 0.05$). The unit-cell parameters of the solid solutions vary little with composition, in accordance with the small difference in ionic radius between gallium and cobalt. The 1100°C section through the phase diagram of the La_2O_3 – Ga_2O_3 – CoO system in air is presented.

DOI: 10.1134/S0020168507070138

INTRODUCTION

LaGaO_3 -based solid solutions possessing high unipolar oxygen-ion conductivity [1, 2] are thought to be candidate materials for solid electrolytes and oxygen sensors. Such solid solutions are also attractive as oxygen separation membranes. Membrane materials must possess high oxygen-ion and electronic conductivities. Doping with transition metals of variable valence, e.g., cobalt, is known to be an effective approach for raising electronic conductivity. Therefore, cobalt-doped lanthanum gallate can be regarded as a potential membrane material.

Practical application of such materials depends on detailed knowledge of their crystal structure, optimal preparation conditions, and the stability limits of the phases involved. According to earlier results [3–6], the compounds existing in the La_2O_3 – Ga_2O_3 – CoO system are the LaCoO_3 and LaGaO_3 perovskites, CoGa_2O_4 spinel, and $\text{La}_4\text{Ga}_2\text{O}_9$. There are, however, no data on the formation of more complex oxides or solid solutions.

The objective of this work was to determine the stability limits of the LaCoO_3 -, LaGaO_3 -, $\text{La}_4\text{Ga}_2\text{O}_9$ -, and CoGa_2O_4 -based solid solutions and to ascertain whether other mixed oxides exist in the system in question.

EXPERIMENTAL

Samples for this investigation were synthesized by a standard ceramic processing technique from oxides and also using the glycine–nitrate combustion process [2] to prepare starting mixtures. The starting reagents used were LaO-D La_2O_3 , extrapure-grade Co_3O_4 , and 99.999+%-pure Ga_2O_3 . To remove adsorbed gases and moisture, the starting reagents were calcined for 3 h:

La_2O_3 at 1200°C, Co_3O_4 at 1000°C (as a result, Co_3O_4 converted to CoO), and Ga_2O_3 at 700°C. Further, two synthetic procedures were used.

In the standard ceramic processing technique, appropriate amounts of the constituent oxides were thoroughly mixed by grinding under ethanol in an agate mortar. The mixtures were fired in three steps, at 950°C for 24 h, then at 1050°C for 24 h, and finally at 1100°C for 168–552 h, with intermediate grindings. The resultant materials were quenched in air. At high gallium contents, the rate of solid-state reactions at 1100°C in air was too slow. For this reason, the gallium-rich samples were heat-treated further, at 1400 and 1200°C, and then at the temperature at which phase equilibria were to be studied, 1100°C.

In the glycine–nitrate combustion process, synthesis was performed as follows: The starting oxides were dissolved in concentrated nitric acid to give approximately 1 M solutions of gallium, cobalt, and lanthanum nitrates. The exact solution concentrations were determined gravimetrically. To this end, a 5-ml sample was boiled down, and the resultant metal nitrate was heated until complete decomposition by gradually raising the temperature to 1000°C. The oxides thus obtained were weighed, and the results were used to determine the exact concentrations of the metal nitrate solutions. Appropriate ratios of the lanthanum, gallium, and cobalt nitrate solutions were then mixed with glycine. The amount of glycine corresponded to the formation of a trimetallic glycine complex with the $[\text{M}(\text{NH}_2\text{CH}_2\text{COO})_3]$ stoichiometry. The resultant glycine–nitrate solution was slowly boiled down. During dehydration, the mixture ignited, leading to the formation of an intermediate product composed of the starting oxides, the compound being synthesized, interme-

Table 1. Unit-cell parameters of $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$

x	a , Å	c , Å	V , Å ³	α , deg	R_{Br} , %	R_{f} , %
0	5.490 (4)	13.497(3)	352.198(2)	120.034(0)	1.59	0.971
0.025	5.490 (3)	13.497(3)	352.338(1)	120.003(0)	1.89	2.11
0.050	5.486 (3)	13.487(3)	351.320(1)	120.058(0)	2.29	1.74

Table 2. Unit-cell parameters of $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$

x	a , Å	c , Å	V , Å ³	α , deg	R_{Br} , %	R_{f} , %
0	5.439(4)	13.084(4)	335.45(2)	120.00(0)	6.30	4.35
0.025	5.440(4)	13.085(4)	335.366(2)	119.998(0)	7.29	5.03
0.050	5.439(4)	13.086(4)	335.267(2)	120.000(0)	6.12	5.40
0.075	5.439(4)	13.086(4)	335.269(2)	120.000(0)	6.07	5.30
0.010	5.440(4)	13.089(3)	335.392(2)	120.000(0)	4.80	3.87

diate phases, and carbon. Next, the mixture was slowly heated to 600°C, held at temperature for 1 h, reground, heat-treated at 850°C for 24 h, reground, heat-treated at 1100°C for 48 h, again reground, and heat-treated at 1200°C for an additional 24 h. The final step of synthesis was heat treatment at 1100°C for 24 h. The final heat-treatment step was needed to study 1100°C phase relations.

All of the samples were quenched to room temperature by withdrawing the crucibles from the hot furnace and cooling them on a massive copper plate. At temperatures from 1100 to 600°C, where solid-state reactions might proceed with considerable rates, the cooling rate was 600°C/min.

The phase composition and crystal structure of the samples were determined by x-ray diffraction (XRD) on a DRON-UM1 powder diffractometer ($\text{CuK}\alpha$ radiation). Unit-cell parameters were refined by the Rietveld profile analysis method.

RESULTS AND DISCUSSION

The phase equilibria in the La_2O_3 – Ga_2O_3 – CoO system were studied at 1100°C in air.

$\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ solid solutions. To determine the limits of the $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ solid-solution series, we prepared samples with $x = 0, 0.025, 0.050, 0.075, 0.100, 0.120, 0.130,$ and 0.150 . The synthesis of the gallate solid solutions by the standard ceramic processing technique was found to require higher firing temperatures and longer times in comparison with the cobaltite solid solutions. At 1100°C (the temperature of the present phase-diagram studies), we failed to obtain phase-pure

lanthanum gallate, even by firing for 500 h. For this reason, the $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ samples were heat-treated in several steps at temperatures of up to 1400°C and then annealed at the temperature of the present phase-diagram studies, 1100°C. The total heat-treatment time was up to 200 h. The glycine–nitrate combustion process made it possible to markedly reduce the firing temperature and time, to 1200°C and 80 h, respectively.

According to XRD results, the $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ samples were single-phase for $x \leq 0.050$, and the $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ samples, for $x \leq 0.100$. Thus, $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ solid solutions exist in the composition range $0 < x \leq 0.050$, and $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ solid solutions exist in the range $0 < x \leq 0.100$.

From XRD data, we determined the cubic cell parameters of the $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ and $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ solid solutions in the hexagonal setting (Tables 1, 2) using standard Fullprof software. The unit-cell parameters were refined in space groups $R3c$ for $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ and $R\bar{3}c$ for $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$.

In both solid-solution systems, the unit-cell parameters vary insignificantly with composition, in accordance with the small difference in ionic radius between Ga^{3+} and Co^{3+} : 0.062 and 0.064 nm, respectively [7].

$\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ solid solutions. To ascertain the existence of $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ solid solutions, we prepared samples with $x = 0, 0.02, 0.04, 0.05, 0.10, 0.15, 0.20,$ and 0.25 . According to XRD data, the $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ solid solutions exist in the composition range $0 < x \leq 0.20$. The $x = 0.25$ sample was mixed-phase. The XRD patterns of the solid solutions ($0 < x \leq 0.20$) and $\text{La}_4\text{Ga}_2\text{O}_9$ could be indexed in a monoclinic unit cell (sp. gr. Pm), using standard Fullprof software.

Table 3. Unit-cell parameters of $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$

x	a , Å	b , Å	c , Å	V , Å ³	β , deg	R_{Br} , %	R_{f} , %
0.00	7.961(7)	11.955(3)	11.562(1)	1042.967(8)	108.305(2)	5.33	4.56
0.05	7.960(4)	11.952(1)	11.558(1)	1042.634(0)	108.305(1)	5.28	3.61
0.10	7.959(1)	11.950(0)	11.548(3)	1042.513(8)	108.347(4)	5.40	3.78
0.15	7.956(7)	11.953(4)	11.532(4)	1042.428(9)	108.793(9)	5.22	3.85
0.20	7.953(2)	10.942(7)	11.432(2)	1042.332(5)	108.113(1)	5.51	4.43

Table 4. Phase fields in the phase diagram of the $\text{La}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$

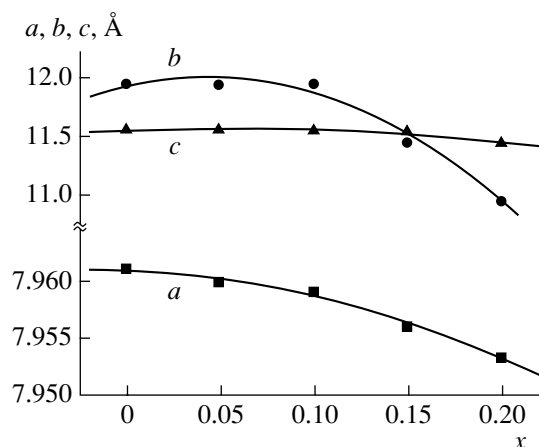
Field	Phase assemblage
<i>I</i>	$\text{LaCo}_{0.9}\text{Ga}_{0.1}\text{O}_3$, La_2O_3 , $\text{La}_4\text{Ga}_{1.8}\text{Co}_{0.2}\text{O}_9$
<i>II</i>	$\text{LaCo}_{0.9}\text{Ga}_{0.1}\text{O}_3$, $\text{La}_4\text{Ga}_{1.8}\text{Co}_{0.2}\text{O}_9$, $\text{LaGa}_{0.95}\text{Co}_{0.05}\text{O}_3$
<i>III</i>	$\text{LaCo}_{0.9}\text{Ga}_{0.1}\text{O}_3$, $\text{Co}_{1.2}\text{Ga}_{1.8}\text{O}_4$, CoO
<i>IV</i>	$\text{LaGa}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{Co}_{1.2}\text{Ga}_{1.8}\text{O}_4$, $\text{LaCo}_{0.9}\text{Ga}_{0.1}\text{O}_3$
<i>V</i>	$\text{LaGa}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{Co}_{1-x}\text{Ga}_{2+x}\text{O}_4$ ($-0.20 \leq x \leq 0.05$)
<i>VI</i>	Ga_2O_3 , $\text{LaGa}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{Co}_{0.95}\text{Ga}_{2.05}\text{O}_4$
<i>VII</i>	$\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.05$), Ga_2O_3
<i>VIII</i>	$\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ ($0 \leq x \leq 0.2$), La_2O_3
<i>IX</i>	$\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ ($0 \leq x \leq 0.2$), $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ ($0 \leq x \leq 0.05$)
<i>X</i>	$\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0 \leq x \leq 0.1$), CoO
<i>XI</i>	$\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ ($0 \leq x \leq 0.1$), La_2O_3

Table 3 lists the unit-cell parameters of the solid solutions, together with the Bragg and profile fit R -factors. The composition dependences of unit-cell parameters for the $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ solid solutions are displayed in Fig. 1.

As seen from Table 3 and Fig. 1, the unit-cell parameters vary insignificantly with composition, which can be accounted for by the small difference in ionic radius between gallium and cobalt, like in the $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ and $\text{LaGa}_{1-x}\text{Co}_x\text{O}_3$ systems.

Homogeneity range of CoGa_2O_4 . To assess the homogeneity range of the compound CoGa_2O_4 , we prepared $\text{Co}_{1-x}\text{Ga}_{2+x}\text{O}_4$ samples with $x = 0, 0.05, 0.10, 0.15$, and 0.20 , and $\text{Co}_{1+y}\text{Ga}_{2-y}\text{O}_4$ samples with $y = 0, 0.05, 0.10$, and 0.20 . Single-phase samples were obtained for $x \leq 0.05$ and $y \leq 0.20$. Thus CoGa_2O_4 dissolves both CoO and Ga_2O_3 . The solid-solution range extends from $\text{Co}_{1.2}\text{Ga}_{1.8}\text{O}_4$ to $\text{Co}_{0.95}\text{Ga}_{2.05}\text{O}_4$. The solubility of cobalt oxide in the spinel phase is higher than that of gallium oxide. The reason for this is that the oxidation state of cobalt changes readily from $2+$ to $3+$, so that excess (superstoichiometric) cobalt can be accommodated on the gallium site since Ga^{3+} and Co^{3+} are

close in ionic radius. In contrast to that of cobalt, the oxidation state of gallium cannot change from $3+$ to $2+$; Accordingly, the degree of gallium substitution on the cobalt site is substantially lower.

**Fig. 1.** Composition dependences of unit-cell parameters for $\text{La}_4\text{Ga}_{2-x}\text{Co}_x\text{O}_9$ solid solutions.

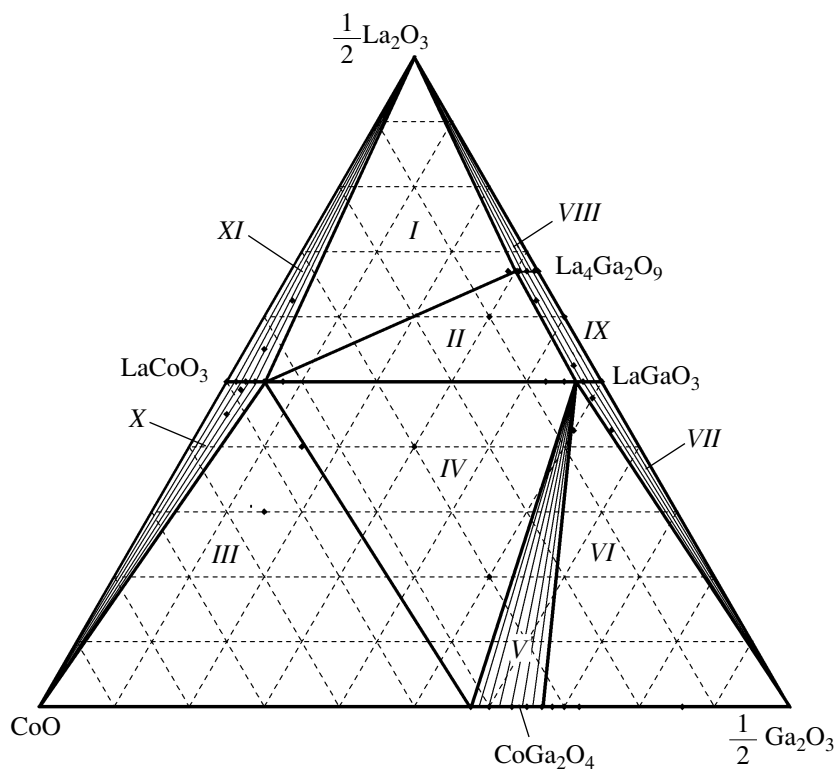


Fig. 2. 1100°C section through the phase diagram of the La_2O_3 - Ga_2O_3 - CoO system in air.

Phase equilibria in the La_2O_3 - Ga_2O_3 - CoO system. Using XRD data for 40 samples, we constructed the 1100°C section of the La_2O_3 - Ga_2O_3 - CoO phase diagram (Fig. 2).

The phase fields in the phase diagram are listed in Table 4.

CONCLUSIONS

We determined the composition ranges and structures of solid solutions in the La_2O_3 - Ga_2O_3 - CoO system at 1100°C in air and constructed the 1100°C section through the phase diagram of the La_2O_3 - Ga_2O_3 - CoO system in air.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant nos. 05-03-32477, 06-08-08120_ofi, and 04-03-96136 Ural).

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