

Phase Equilibria in the LaCoO_3 – LaMnO_3 – BaCoO_z – BaMnO_3 System

V. A. Cherepanov,^{*,1} E. A. Filonova,^{*} V. I. Voronin,[†] and I. F. Berger[‡]

^{*} Department of Chemistry, Ural State University, Lenin av. 51, Ekaterinburg, 620083, Russia; [†] Institute for Metal Physics, Ural Branch of RAS, S. Kovalevskaya st. 18, Ekaterinburg, GSP-170, 620219, Russia; and [‡] Institute of Solid State Chemistry, Ural Branch of RAS, Pervomaiskaia st. 91, Ekaterinburg, GSP-145, 620219, Russia

Received October 13, 1999; in revised form February 9, 2000; accepted April 20, 2000; published online August 3, 2000

The phase equilibria in the LaCoO_3 – LaMnO_3 – BaCoO_z – BaMnO_3 system were studied at 1100°C in air by powder X-ray diffractometry of quenched samples. The existence of three phases in the $\text{BaCo}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ system was confirmed. Two of these phases are homogeneous in the range $0.15 \leq y \leq 0.30$ and $0.38 \leq y \leq 0.55$. Both have hexagonal structures (space group $P6_3/mmc$), but 10-layered and 12-layered cells, respectively. The last phase, with approximate composition $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$, was indexed on the basis of a $21H$ -structure with the unit cell parameters $a = 5.7676(8)$ and $c = 49.58(1)$ Å (space group $P6_3/mmc$). It was found that $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3\pm\delta}$ phases with $0 \leq x \leq 0.10$ possess O -orthorhombic structures (space group $Pnma$) and samples with $0.125 \leq x \leq 0.30$ have rhombohedral structures (space group $R\bar{3}c$). The homogeneity range of solid solutions of the general formula $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ with orthorhombic, rhombohedral, and cubic structures has been determined. On the basis of the experimental results and earlier data, the pseudoquaternary phase diagram at 1100°C in air was constructed. © 2000 Academic Press

studied earlier. It is well known that at 1100°C in air, LaCoO_3 possesses rhombohedrally distorted (2) and $\text{LaMnO}_{3+\delta}$ orthorhombically distorted (3) perovskite-type structures. A number of phases with the general formula BaCoO_z are described in (4–11). The crystal structure and oxygen content of BaCoO_z strongly depend on the temperature and oxygen pressure used for preparation. Low-temperature hexagonal ($2H$) structures (4, 10, 11) transformed into different polytypes, such as $5H$ with $z = 2.78$ (7) or $12H$ with $z = 2.6$ (5, 6), while it lost oxygen with temperature increase or oxygen pressure decrease. BaMnO_3 with hexagonal $2H$ structure (space group $P6_3/mmc$) can be obtained in air at relatively low temperature or high oxygen pressure (12–18). The increase of temperature or decrease of oxygen pressure leads to the formation of a number of oxygen-deficient $\text{BaMnO}_{3-\delta}$ phases with perovskite-related structure which can be described as $15H$ -, $8H$ -, $6H$ -, $10H$ -, and $4H$ -polytypes (12, 17), $21R$ -, $27R$ -, $33R$ -polytypes (16), and $21R$ -polytype (18).

INTRODUCTION

Perovskite-type oxides, based on rare earth and $3d$ transition elements, were found to be promising materials for use as electrodes, catalysts, membranes, and so on. A traditional way of modifying the properties of materials is by partial substitution of components in different sublattices. The phase equilibria and crystal structure of lanthanum cobaltate partially substituted by strontium in the La sublattice and by manganese in the Co sublattice were studied recently (1). The aim of the present investigation is to study the phase equilibria in the LaCoO_3 – LaMnO_3 – BaCoO_z – BaMnO_3 system at 1100°C in air and determine the crystal structure of the single phases formed.

Individual components of the system under investigation and phase equilibria in the quasibinary systems were

LaCoO_3 – LaMnO_3 System

The phase diagram of the LaCoO_3 – LaMnO_3 system in air has been constructed by Jonker (19). According to his data, partial solid solubility occurs in the system: $\text{LaCo}_{1-y}\text{Mn}_y\text{O}_3$ with a rhombohedral structure formed in the range $0 \leq y \leq 0.12$ and that with an orthorhombic structure formed in the range $0.55 \leq y \leq 1$. Other information in the literature relates to different experimental conditions. According to Goodenough *et al.* (20), the immiscibility range occurs at $0.4 \leq y \leq 0.6$ at 1573 K. The homogeneity range of solid solution with orthorhombic structure in pure oxygen at 1273 K was found to be $0 \leq y \leq 0.4$ (21), $0 \leq y \leq 0.6$ (22), and $0 \leq y \leq 0.25$ (23). Our recent study of this system by means of XRD and neutron diffraction of samples quenched from 1373 K in air shows the existence of solid solutions with rhombohedral structures over the range $0 \leq y \leq 0.28$ and with orthorhombic structures over the range $0.5 \leq y \leq 1$ (24). The wider ranges of solubility obtained in (24) in comparison with

¹ To whom correspondence should be addressed.

those of Jonker (19) can be explained by the use of longer equilibration time: about 5 days with intermediate grinding in (24) and 3–5 hrs in (19).

LaCoO₃–BaCoO₂ System

A recent detailed investigation of the La–Ba–Co–O system leads to the conclusion that the homogeneity range of the La_{1–x}Ba_xCoO_{3–δ} solid solution at 1373 K in air is $0 \leq y \leq 0.8$ (25). It was found that rhombohedral distortions of the perovskite-type structure of LaCoO₃ decrease as the barium content increases. La_{0.5}Ba_{0.5}CoO_{3–δ} possessed the ideal cubic structure.

LaMnO₃–BaMnO₃ System

Formation of a solid solution in the LaMnO₃–BaMnO₃ system was shown in (26–31). The homogeneity range of La_{1–x}Ba_xMnO_{3±δ} depends on temperature: the limiting composition (x) was equal to 0.3 at 900°C according to (26), while the single phase with $x = 0.4$ was obtained at 600–1350°C (27), and Jonker found $x = 0.5$ at 1200–1400°C (28, 29). It was shown that the crystal structure of La_{1–x}Ba_xMnO_{3±δ} depends on the oxygen content, i.e., concentration of Mn⁴⁺ ions. Orthorhombic O' or O phases were obtained for samples with Mn⁴⁺ concentration lower than 12% (30, 31). The increase of Mn⁴⁺ concentration leads to formation of either the rhombohedral ($R\bar{3}c$) or cubic ($Pm\bar{3}m$) phase.

BaCoO₂–BaMnO₃ System

Phase formation in this system has been studied only in an atmosphere of pure oxygen by Taguchi *et al.* (32). They

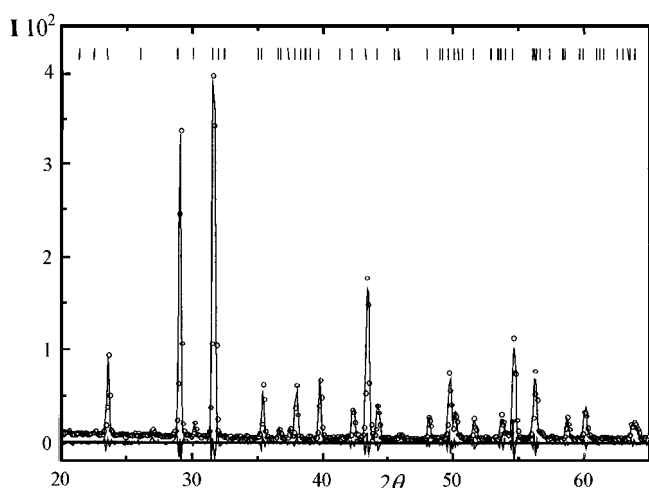


FIG. 1. X-ray powder diffraction pattern for BaCo_{0.8}Mn_{0.2}O_{3–δ}. (Observed plot is shown by circles, calculated plot by solid line. Difference plot appears below. The vertical lines mark reflections.)

TABLE 1
XRD Data for the Single Phase Samples

BaCo _{0.8} Mn _{0.2} O _{3–δ}				BaCo _{0.6} Mn _{0.4} O _{3–δ}			
<i>h k l</i>	<i>l</i>	<i>d</i> , Å	<i>I/I</i> ⁰ , (%)	<i>h k l</i>	<i>l</i>	<i>d</i> , Å	<i>I/I</i> ⁰ , (%)
1 0 4	4	3.788	18	1 0 4	4	4.051	5
1 0 6	6	3.085	79	1 0 5	5	3.727	12
1 1 0	0	2.839	100	1 0 6	6	3.420	9
1 0 8	8	2.543	13	1 0 7	7	3.139	74
0 0 10	10	2.377	13	1 0 8	8	2.888	14
2 0 4	4	2.272	17	0 0 10	10	2.852	8
1 0 10	10	2.140	9	1 1 0	0	2.842	100
2 0 6	6	2.089	47	1 0 10	10	2.468	9
1 1 8	8	2.052	10	0 0 12	12	2.377	9
2 0 8	8	1.892	8	2 0 5	5	2.260	19
2 1 2	2	1.836	20	2 0 6	6	2.186	59
2 1 3	3	1.834	5	1 0 12	12	2.141	9
1 1 10	10	1.822	8	2 0 8	8	2.026	6
2 1 4	4	1.774	6	1 1 10	10	2.013	8
2 0 10	10	1.709	6	1 0 14	14	1.883	11
2 1 6	6	1.682	30	2 1 0	0	1.864	5
3 0 0	0	1.639	21	1 1 12	12	1.823	6
2 1 8	8	1.575	8	2 0 12	12	1.710	10
2 0 12	12	1.541	11	2 1 7	7	1.6932	28
2 1 10	10	1.464	5	2 1 8	8	1.650	5
				3 0 0	0	1.641	24
				2 0 14	14	1.570	7
				2 1 12	12	1.465	7

found complete miscibility at 600°C. All BaCo_{1–y}Mn_yO₃ solid solutions had 2H-type structures. We have not found any information about phase equilibria in this system in air.

EXPERIMENTAL

Lanthanum oxide (La₂O₃, 99.99% purity), barium carbonate (BaCO₃), manganese oxide (Mn₂O₃), and cobalt oxide (Co₃O₄) of “pure for analysis” or “special purity” grade were used as starting materials. All were dried: La₂O₃ at 1200°C, Mn₂O₃ and Co₃O₄ at 700°C, and BaCO₃ at 500°C. Samples were prepared by mixing the reactants in appropriate ratios, ground in an agate mortar, and fired in

TABLE 2
Unit Cell Parameters of BaCo_{1–y}Mn_yO_{3–δ} with 10H-Structure

	<i>y</i>			
	0.15	0.20	0.25	0.30
<i>a</i> _{hex} , Å	5.6706(7)	5.6737(4)	5.6703(5)	5.6757(5)
<i>c</i> _{hex} , Å	23.758(4)	23.752(2)	23.735(3)	23.747(4)
<i>V</i> , Å ³	661.623	662.153	660.878	662.482
<i>R</i> _f	3.86	2.02	4.67	3.81
<i>R</i> _{Br}	3.46	2.31	3.44	3.81

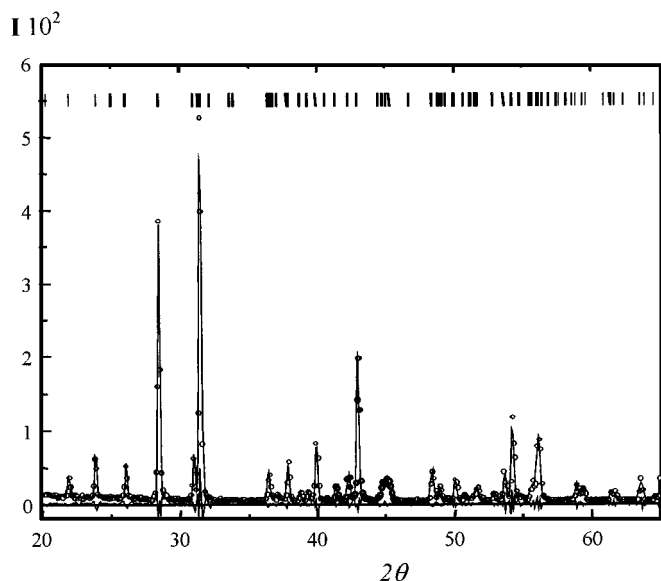


FIG. 2. X-ray diffraction pattern for BaCo_{0.6}Mn_{0.4}O_{3- δ} . (Observed plot is shown by circles, calculated plot by solid line. Difference plot appears below. The vertical lines mark reflections.)

air at 850°C for 24 hrs, at 950°C for 24 hrs, and finally at 1100°C for 120–160 hrs with intermediate grinding in alcohol after every 20 hrs. After each stage, the powder samples in alumina crucibles were quenched to room temperature on a cold, massive copper plate. The time required to cool samples from 1100°C to about 600°C (the temperature at which all phase transformations in such systems are extremely slow) was about 15 seconds. This means that the cooling rate used for quenching was about 2000 deg/min.

In order to identify the phase compositions, all samples were examined by X-ray diffraction, using a DRON-3 diffractometer with CuK α_1 radiation. For Rietveld analysis, intensity data were collected at each $2\theta = 0.05$ step for 10 seconds over a 2θ angular range $10 < 2\theta < 100^\circ$. The equilibrium state was considered to be reached when the phase composition (i.e., X-ray patterns) remained unchanged during the last few stages of firing. Obtained data

TABLE 3
Unit Cell Parameters of BaCo_{1-y}Mn_yO_{3- δ} with 12H-Structure

	y				
	0.38	0.40	0.45	0.50	0.55
$a_{hex}, \text{\AA}$	5.6829(5)	5.6852(6)	5.6880(4)	5.6906(3)	5.6921(5)
$c_{hex}, \text{\AA}$	28.528(3)	28.523(3)	28.545(2)	28.539(2)	28.537(3)
$V, \text{\AA}^3$	797.882	798.407	799.822	800.348	800.705
R_f	2.93	3.00	2.57	2.60	2.89
R_{Br}	3.24	2.72	2.12	2.36	4.90

TABLE 4
Structural Parameters of the La_{1-x}Ba_xMnO_{3 \pm δ} with Orthorhombic Structure (in Hexagonal Setting)

	x			
	0.000	0.050	0.075	0.100
$a_{orts}, \text{\AA}$	5.4820(9)	5.5079(5)	5.5079(7)	5.476(2)
$b_{orts}, \text{\AA}$	7.778(2)	7.7948(7)	7.816(2)	7.786(3)
$c_{orts}, \text{\AA}$	5.5253(9)	5.5463(4)	5.5516(8)	5.523(2)
$V, \text{\AA}^3$	235.601	238.086	238.982	235.447
La: x	0.5184(8)	0.4846(7)	0.488(1)	0.513(2)
z	0.007(2)	-0.0021(4)	-0.001(3)	0.003(6)
O1: x	-0.005(7)	0.011(6)	0.006(8)	-0.01(2)
z	0.075(1)	0.059(9)	0.050(2)	0.05(3)
O2: x	0.288(9)	0.273(7)	0.276(7)	0.29(1)
y	0.096(9)	-0.036(4)	-0.039(6)	0.04(1)
z	0.23(2)	0.25(1)	0.27(1)	0.26(2)

were refined by the Rietveld profile method using the “DBWS9411” and “Fullprof” programs.

RESULTS AND DISCUSSION

Because the BaCoO₂-BaMnO₃ system had not been studied previously in air and the homogeneity range of La_{1-x}Ba_xMnO_{3 \pm δ} was not clear at 1100°C in air, preliminary investigations on these system were undertaken.

Phase Equilibria in the BaCoO_{2.5}-BaMnO₃ Systems

Samples of the general composition BaCo_{1-y}Mn_yO_{3- δ} ($0 \leq y \leq 1$) in steps of 0.05, except the range $0.70 \leq y \leq 0.75$, where the step was 0.01, were prepared and annealed according to the scheme described above.

According to XRD a single phase with hexagonal 10H-structure (space group $P6_3/mmc$) was found in the range $0.15 \leq y \leq 0.30$. Experimental and calculated XRD patterns for BaCo_{0.8}Mn_{0.2}O_{3- δ} are shown in Fig. 1. X-ray diffraction data for BaCo_{0.8}Mn_{0.2}O_{3- δ} are listed in Table 1. The unit cell parameters for the single phase samples with different compositions ($0.15 \leq y \leq 0.30$) are listed in Table 2. All samples with $y < 0.15$ contained BaCoO₂ as a second phase, which was indexed on the basis of 12H-structure (space group $P\bar{6}m2$) with unit cell parameters $a = 5.672(2)$ and $c = 28.58(1)$ \AA.

All samples inside the range $0.38 \leq y \leq 0.55$ were identified as single phase and indexed on the basis of 12H-structure (space group $P6_3/mmc$). A typical profile of this phase is shown in Fig. 2. XRD data for the sample with $y = 0.4$ are listed in Table 1. The unit cell parameters for the single phase samples with different composition ($0.38 \leq y \leq 0.55$) are listed in Table 3.

TABLE 5
Structural Parameters of the $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3\pm\delta}$ with Rhombohedral Structure

	x						
	0.125	0.150	0.180	0.200	0.225	0.250	0.300
$a_{\text{hex}}, \text{\AA}$	5.5522(4)	5.5432(4)	5.5485(4)	5.5444(5)	5.5433(5)	5.5398(5)	5.5323(5)
$c_{\text{hex}}, \text{\AA}$	13.429(1)	13.425(1)	13.453(1)	13.465(1)	13.471(1)	13.475(1)	13.495(2)
$V, \text{\AA}^3$	358.527	357.244	358.667	358.457	358.485	358.147	357.687
O: x	0.548(3)	0.456(3)	0.453(3)	0.537(1)	0.462(3)	0.462(3)	0.476(5)

XRD patterns of all samples inside the composition range $0.3 \leq y < 0.38$ were sets of reflections of two phases with limiting composition: $\text{BaCo}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ and $\text{BaCo}_{0.62}\text{Mn}_{0.38}\text{O}_{3-\delta}$.

XRD patterns of all samples with $0.55 < y < 1$ show the existence of one more phase in this system. Unfortunately, we could not obtain a single phase sample. All samples inside the $0.55 < y \leq 0.71$ range contained $\text{BaCo}_{0.45}\text{Mn}_{0.55}\text{O}_{3-\delta}$ as a second phase and samples with $0.72 \leq y \leq 0.98$ contained BaMnO_3 as a second phase. Thus, we suggest that the new phase appears in the vicinity of $y \sim 0.71-0.72$. This new phase with approximate average composition $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$ was indexed on the basis of $21H$ -structure with unit cell parameters $a = 5.7676(8)$ and $c = 49.58(1) \text{\AA}$ (space group $P6_3/mmc$). Determination of the detailed crystal structure and the preparation route of the single phase sample should be the subject of a special investigation. It is difficult to obtain multilayer compounds as a single phase (such as 21-, 27-, and 33-layered and others) because of possible intergrowth (18).

BaMnO_3 obtained as a single phase and in the mixtures with $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$ in the sample with $y \geq 0.72$ has a $2H$ -structure (space group $P6_3/mmc$) with unit cell parameters $a = 5.6944(7)$ and $c = 4.8125(8) \text{\AA}$ which is in good agreement with (10, 12, 18).

Phase Equilibria in the LaMnO_3 - BaMnO_z System

A number of samples of general composition $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3\pm\delta}$ were prepared and annealed according to the scheme described above.

According to the results of XRD single phase samples were obtained in air at 1100°C for $0 \leq x \leq 0.30$ which is in good agreement with (26, 27). All samples with $x > 0.3$ contained BaMnO_3 as a second phase.

It was shown that $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3\pm\delta}$ phases with $0 \leq x \leq 0.10$ possess the O -orthorhombic structure (space group $Pnma$). Structural parameters are listed in Table 4. The samples with $0.125 \leq x \leq 0.30$ has a rhombohedral structure (space group $R\bar{3}c$). The unit cell parameters in hexagonal setting are listed in Table 5.

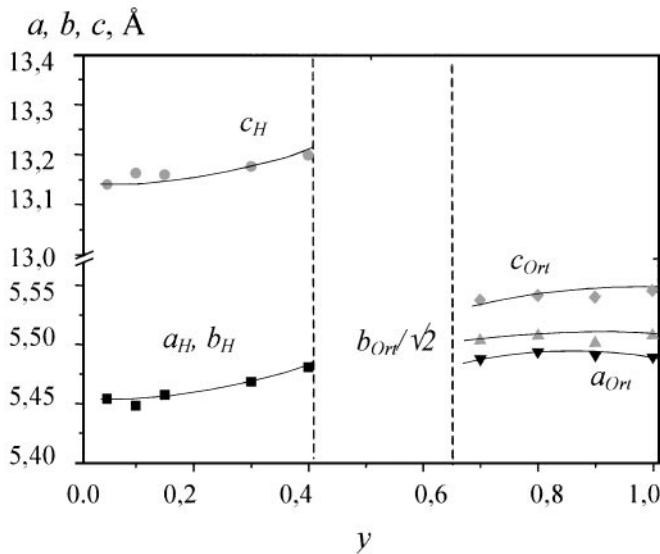


FIG. 3. Unit cell parameters of $\text{La}_{0.95}\text{Ba}_{0.05}\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ with rhombohedral and orthorhombic structure.

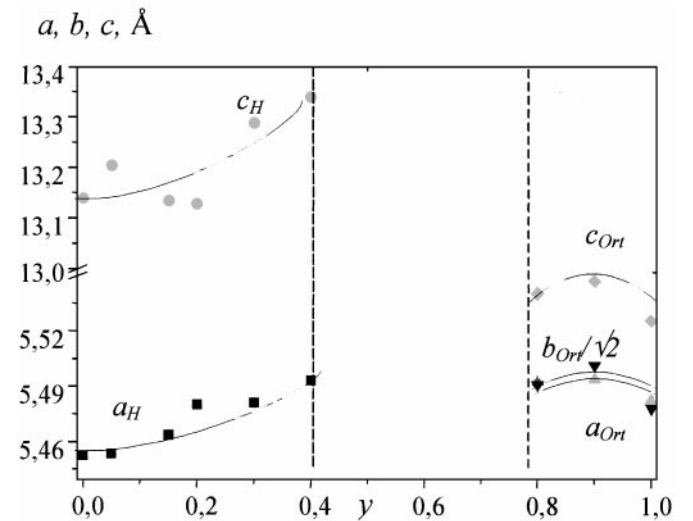


FIG. 4. Unit cell parameters of $\text{La}_{0.9}\text{Ba}_{0.1}\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ with rhombohedral and orthorhombic structure.

TABLE 6
Unit Cell Parameters of the La_{0.95}Ba_{0.05}Co_{1-y}Mn_yO_{3±δ} Solid Solutions

	y							
	0.05	0.1	0.15	0.3	0.4	0.7	0.8	0.9
a, Å	5.4481(1)	5.454(1)	5.4574(2)	5.4683(2)	5.4807(1)	5.5032(8)	5.5073(2)	5.494(1)
b, Å	—	—	—	—	—	7.792(1)	7.8009(2)	7.784(1)
c, Å	13.140(2)	13.163(3)	13.159(2)	13.175(8)	13.197(9)	5.538(1)	5.542(4)	5.5392(9)

Phase Equilibria in LaCoO₃-LaMnO₃-BaCoO₂-BaMnO₃ System

Because 3d transition metals can have different oxidation states in simple and complex oxides under the same conditions, and they can be easily changed while the composition given by x and y in La_{1-x}Ba_xCo_{1-y}Mn_yO_{3±δ}, changes, for the sake of simplicity, the oxygen content in condensed phases is not be taken into account in all following composition representations and analysis.

It is well known that the representation of four-component systems even at constant temperature and pressure has to be three-dimensional. The traditional representation is as a composition tetrahedron. In our case, it is more convenient to consider the pure metals or cations as the components. Therefore, the phase diagram is based on the relative mole fraction of the metals, such as $\xi_{\text{Co}} = n_{\text{Co}} / (n_{\text{La}} + n_{\text{Ba}} + n_{\text{Mn}} + n_{\text{Co}})$. Each apex of the tetrahedron represents a pure component, each edge represents a binary system, and each triangle represents a ternary system. All ABO_{3±δ} phases are located at the middle of each edge of the tetrahedron. They belong to one plane, which represents a square pseudoquaternary cross section of the phase diagram. Each apex of the square represents a single ABO_{3±δ} phase and each side a quasibinary system ABO_{3±δ}-A'B'O_{3±δ}. In terms of the La_{1-x}Ba_xCo_{1-y}Mn_yO_{3±δ} composition each pair of parallel sides show a variation of x and y respectively. This is the traditional and convenient way to represent such systems, sometimes called “reciprocal (or mutual) systems”.

XRD patterns of about 50 samples with different compositions inside the pseudoquaternary section show that the structure and homogeneity range of La_{1-x}Ba_xCo_{1-y}Mn_yO_{3±δ} depend significantly on the values of x and y . The samples La_{0.95}Ba_{0.05}Co_{1-y}Mn_yO_{3±δ} and La_{0.9}Ba_{0.1}Co_{1-y}Mn_yO_{3±δ} in the range $0 \leq y \leq 0.4$ had a rhombohedrally distorted perovskite structure similar to that of LaCoO₃ (space group $R\bar{3}c$). The samples La_{0.95}Ba_{0.05}Co_{1-y}Mn_yO_{3±δ} in the range $0.7 \leq y \leq 1$ and La_{0.9}Ba_{0.1}Co_{1-y}Mn_yO_{3±δ} in the range $0.8 \leq y \leq 1$ had orthorhombic structures similar to that of LaMnO_{3±δ} (space group $Pnma$). The unit cell parameters versus composition are shown in Figs. 3 and 4 and listed in Tables 6 and 7. Two phase regions, where rhombohedral and orthorhombic phases coexisted, were found at $0.4 < y < 0.7$ for $x = 0.05$ and $0.4 < y < 0.8$ and $x = 0.1$.

The crystal structure of La_{0.8}Ba_{0.2}Co_{1-y}Mn_yO_{3±δ} was found to be rhombohedral for all values of y (space group $R\bar{3}c$). It is in good agreement with the orthorhombic \leftrightarrow rhombohedral transition found in La_{1-x}Ba_xMnO_{3±δ} at 1100°C in air between $x = 0.1$ and $x = 0.125$. The unit cell parameters for these compositions are listed in Table 8. In all cases the unit cell parameters increase with y because the ionic radius of Mn³⁺ (0.58 Å) is larger than that of Co³⁺ (0.525 Å) (31).

La_{1-x}Ba_xCo_{1-y}Mn_yO_{3±δ} samples with composition (x and y values) in the vicinity of La_{1-x}Ba_xCoO_{3-δ} where $0.5 \leq x \leq 0.8$ (which was found to be cubic earlier (25)) are cubic (space group $Pm\bar{3}m$), Table 9. We have not found any two-phase region between the fields of rhombohedral and

TABLE 7
Unit Cell Parameters of the La_{0.9}Ba_{0.1}Co_{1-y}Mn_yO_{3±δ} Solid Solutions

	y						
	0.05	0.15	0.2	0.3	0.4	0.8	0.9
a, Å	5.4534(7)	5.464(2)	5.480(1)	5.481(1)	5.493(1)	5.492(1)	5.484(1)
b, Å	—	—	—	—	—	7.797(2)	7.787(2)
c, Å	13.204(2)	13.134(4)	13.126(3)	13.288(5)	13.340(4)	5.540(1)	5.532(1)

TABLE 8
Unit Cell Parameters of the $\text{La}_{0.8}\text{Ba}_{0.2}\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ Solid Solutions

	y				
	0.1	0.3	0.5	0.7	0.9
$a_{\text{hex}}, \text{\AA}$	5.4656(8)	5.470(1)	5.4959(1)	5.5134(9)	5.5359(2)
$c_{\text{hex}}, \text{\AA}$	13.284(2)	13.326(5)	13.371(5)	13.421(3)	13.4388(3)

cubic solid solutions. All other Ba-rich samples were multi-phase (two-phase or three-phase) mixtures.

The results of phase composition analysis of all samples combined with literature data on phase equilibria in

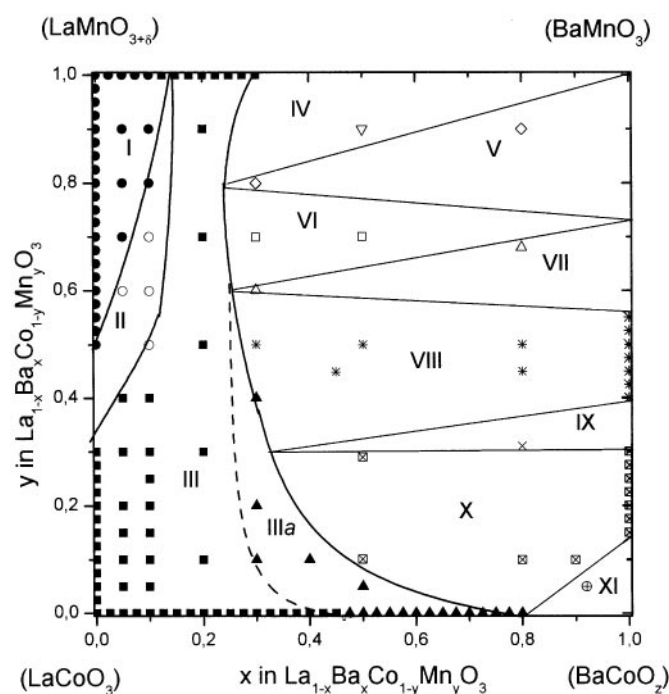


FIG. 5. Phase diagram of the LaCoO_3 - LaMnO_3 - BaCoO_2 - BaMnO_3 system at 1100°C in air. Points represent the samples. Different shapes of the points correspond to different phase composition, marked by Roman numerals as follows: I, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with orthorhombic structure; II, mixture of orthorhombic and rhombohedral s.s.; III, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with rhombohedral structure; IIIa, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with cubic structure; IV, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{O}_{3\pm\delta}$ s.s. + BaMnO_3 ; V, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with fixed composition + BaMnO_3 + $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$; VI, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. + $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$; VII, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with fixed composition + $\text{BaCo}_{0.285}\text{Mn}_{0.715}\text{O}_{3-\delta}$ + $\text{BaCo}_{0.45}\text{Mn}_{0.55}\text{O}_{3-\delta}$; VIII, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with rhombohedral structure or with cubic structure + $\text{BaCo}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ with $0.38 \leq y \leq 0.55$; IX, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with fixed composition + $\text{BaCo}_{0.62}\text{Mn}_{0.38}\text{O}_{3-\delta}$ + $\text{BaCo}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$; X, $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ s.s. with cubic structure + $\text{BaCo}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ with $0.15 \leq y \leq 0.30$; XI, $\text{La}_{0.2}\text{Ba}_{0.8}\text{CoO}_{3-\delta}$ + $\text{BaCo}_{0.85}\text{Mn}_{0.15}\text{O}_{3-\delta}$ + BaCoO_2 .

TABLE 9
Unit Cell Parameters of the $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ Solid Solutions with Cubic Structure

	0.3	0.3	0.3	0.4	0.5
x	0.3	0.3	0.3	0.4	0.5
y	0.1	0.2	0.4	0.1	0.05
a, \AA	3.867(1)	3.8703(6)	3.8777(8)	3.8731(8)	3.8749(6)

quasibinary systems allowed the pseudoquaternary section square of the phase diagram to be divided into 12 fields (Fig. 5). Fields I and III represent the single phase solid solutions of general formula $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ with orthorhombic (I) and rhombohedral (III) or cubic (IIIa) structure, respectively. One can assume that a two-phase region between rhombohedral and cubic phases has the shape of a triangle, but is probably very narrow. We also have not divided the two-phase field VIII into two parts, because it is not easy to determine the exact compositions of $\text{La}_{1-x}\text{Ba}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3\pm\delta}$ and $\text{BaCo}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ in these mixtures.

ACKNOWLEDGMENTS

This work has been supported in part by grants from the Russian Basic Science Foundation, Nos. 97-02-17315 and 97-03-33632.

REFERENCES

- V. A. Cherepanov, E. A. Filonova, V. I. Voronin, I. F. Berger, and L. Yu. Barkhatova, *Mater. Res. Bull.* **34**, 1481 (1999).
- A. N. Petrov, O. F. Kononchuk, A. V. Andreev, V. A. Cherepanov, and P. Kofstad, *Solid State Ionics* **80**, 189 (1995).
- V. A. Cherepanov, L. Yu. Barkhatova, and V. I. Voronin, *J. Solid State Chem.* **134**, 38 (1997).
- T. Negas and R. S. Roth, *Nat. Bur. Stand. Spec. Publ.* **364**, 233 (1972) (*Solid State Chem., Proc. 5th Mater. Res. Symp.*, July 1972).
- A. J. Jacobson and J. L. Hutchison, *J. Solid State Chem.* **35**, 334 (1980).
- A. J. Jacobson and J. L. Hutchison, *J. Chem. Soc., Chem. Commun.* 116 (1976).
- M. Parras, A. Varela, H. Seehofer, and J. M. Gonzalez-Calbet, *J. Solid State Chem.* **120**, 327 (1995).
- B. V. Lazarev and I. S. Shaplygin, *Izv. Akad. Nauk SSSR Nergan. Mater.* **14**, 58 (1982) (in Russian).
- O. V. Godgieva, N. V. Porotnikov, G. E. Nikiforova, and E. A. Tishenko, *Russ. J. Inorg. Chem.* **35**, 44 (1990) (in Russian).
- B. E. Gushee, L. Katz, and R. Ward, *J. Am. Chem. Soc.* **79**, 5601 (1957).
- M. Zanne, A. Courtois, and C. Gleitzer, *Bull. Soc. Chim. Fr.* **12**, 4470 (1972).
- T. Negas and R. S. Roth, *J. Solid State Chem.* **3**, 323 (1971).
- M. Nobuasu, H. Kao, K. Akio, and K. Masanori, *J. Chem. Soc. Jpn.* **74**, 1094 (1971).
- B. L. Chamberland, A. W. Sleight, and J. F. Weither, *J. Solid State Chem.* **1**, 506 (1970).
- Y. Syono and S. Akimoto, *J. Phys. Soc. Jpn.* **2**, 994 (1969).
- J. M. Gonzalez-Calbet, M. Parras, J. Alonso, and M. Vallet-Rigi, *J. Solid State Chem.* **111**, 202 (1994).
- K. Uematsu, K. Kuroda, N. Mizutani, and M. Kato, *J. Am. Ceram. Soc.* **60**, 466 (1977).

18. M. Parras, J. M. Gonzalez-Calbet, J. Alonso, and M. Vallet-Rigi, *J. Solid State Chem.* **113**, 78 (1994).
19. G. H. Jonker, *J. Appl. Phys.* 1424 (1966).
20. J. B. Goodenough, A. Wold, R. J. Arnett, and N. Menyuk, *Phys. Rev.* **124**, 373 (1961).
21. V. Narasimhan, K. Seshan, D. K. Chakrabarty, and H. V. Keer, *Phys. Stat. Sol. A* **70**, 155 (1982).
22. V. Narasimhan, D. Y. Rao, D. K. Chakrabarty, and H. V. Keer, *J. Indian Chem. Soc.* **110**, 197 (1983).
23. E. F. Bertaut and F. Forrat, *J. Phys. Radium* **17**, 129, (1956).
24. E. A. Filonova, V. A. Cherepanov, and V. I. Voronin, *Russ. J. Phys. Chem.* **72**, 1876 (1998).
25. V. A. Cherepanov, L. Ya. Gavrilova, E. A. Filonova, M. V. Trifonova, and V. I. Voronin, *Mater. Res. Bull.* **34**, 983 (1999).
26. J. Orehotsky and J. L. Orehotsky, *IEEE. Trans. Magn.* **19**, 1969 (1983).
27. A. Chakraborty, P. S. Devi, and H. S. Maiti, *J. Mater. Sci.* **10**, 918 (1995).
28. G. H. Jonker and J. H. van Santen, *Physica* **3**, 337 (1950).
29. G. H. Jonker, *Physica* **22**, 707 (1956).
30. J. B. A. Elemans, B. van Laar, K. R. van der Veen, and B. O. Loopstra, *J. Solid State Chem.* **3**, 238 (1971).
31. M. C. Martin, G. Shirane, Y. Endoh, K. Hirota, Y. Morimoto, and Y. Tokura, *Phys. Rev. B.* **53**, 14285 (1996).
32. H. Taguchi, M. Shimada, F. Kanamaru, M. Koizumi, and Y. Takeda, *J. Solid State Chem.* **18**, 299 (1976).