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Mechanochemical Synthesis and Physicochemical Properties of $La_{1-x}Ba_xFeO_{3-\delta}$ $(0 \le x \le 1)$ Perovskites

L. A. Isupova[a], A. N. Nadeev[a], I. S. Yakovleva[a], and S. V. Tsybulya[b]
[a] Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
[b] Novosibirsk State University, Novosibirsk, 630090 Russia
e-mail: nadeev@catalysis.ru

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Abstract—$La_{1-x}Ba_xFeO_{3-\delta}$ (x = 0–1) perovskites were prepared by the mechanical activation of mixtures of binary oxides in a centrifugal planetary ball mill for 3 min followed by calcination at 1100°C for 4 h, and their phase composition was determined by X-ray diffraction. All samples up to $x = 0.8$ are single-phase oxides with a perovskite structure. The $x = 1$ sample is a mixture of perovskite- and brownmillerite-type phases. An orthorhombic-to-cubic morphotropic transition is observed at $x = 0.3$. The catalytic activity of the perovskite samples in CO oxidation, chosen as a model reaction, depends nonmonotonically on the barium content of the catalyst. High catalytic activities are shown by the $x = 0.8$ and 0.3 samples.

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Due to their stability at high temperatures and unique physicochemical properties, solid solutions based on lanthanum ferrite are usable as oxygen-permeable membranes for high-temperature cathodes in solid-oxide fuel cells [1] and as total oxidation catalysts [2]. Oxides with a perovskite structure can replace catalysts based on noble metals in some high-temperature catalytic oxidation processes (gas cleaning, high-temperature methane conversion, and ammonia oxidation) since they are more stable in reaction media and are comparatively cheap [3–5]. The catalytic properties of perovskite-type oxides are known to depend on the transition metal and its coordination environment and charge [6]. In turn, the properties of perovskite-based solid solutions are governed by the nature of the substituent cation and the degree of substitution [7] and may depend on the preparation procedure.

Mechanochemical synthesis is a wasteless technology for obtaining mixed oxides with a large specific surface area. As compared to conventional solid-phase synthesis, it requires lower temperatures and shorter subsequent heat treatment times. These features make mechanochemical synthesis promising for producing catalysts, including perovskite-type mixed oxides. In this method, the starting reactants are mechanically treated in a high-energy mill and then heat-treated.

The mechanochemical method was earlier used in the synthesis of $La_{1-x}A_xFeO_{3-\delta}$ (A = Ca, Sr) solid solutions, and the resulting series of products had some specific features differentiating them from ceramic materials [2, 8–10].

For example, in an earlier paper [8], we noted the specific features of $La_{1-x}Ca_xFeO_{3-\delta}$ samples prepared by the mechanochemical and ceramic methods. According to X-ray diffraction data, all mechanochemically synthesized samples were two-phase and consisted of perovskite and brownmillerite. According to electron microscopy data, these phases in some samples formed nanocomposites that consisted of a perovskite "core" and a calcium-enriched brownmillerite "shell." We believe that it is this microstructure that is responsible for the catalytic activity of these materials.

The $La_{1-x}Sr_xFeO_{3-\delta}$ system forms solid solutions and undergoes a morphotropic transition at $x \sim 0.3$ [9–11]. Among the mechanochemically synthesized materials [9], the $x = 0.3$ and 0.4 samples are two-phase, have a disordered microdomain structure, and show the highest catalytic activity in CO oxidation.

The equilibrium phase diagram of the $La_{1-x}Ba_xFeO_{3-\delta}$ system is known [12]. The symmetry of the crystal structure in the system changes from orthorhombic ($0 \le x \le 0.25$) to cubic ($0.25 < x \le 0.66$). For $0.66 < x \le 0.99$, the system is two-phase, consisting of the cubic phase of perovskite and the monoclinic phase of brownmillerite ($Ba_2Fe_2O_5$) [12]. The mechanochemical synthesis of this system can yield persistent metastable states or composites potentially interesting for their special properties, including catalytic activity.

Here, we report specific structural features of a series of mechanochemically synthesized $La_{1-x}Ba_xFeO_{3-\delta}$ samples and the catalytic activity of these samples in CO oxidation.

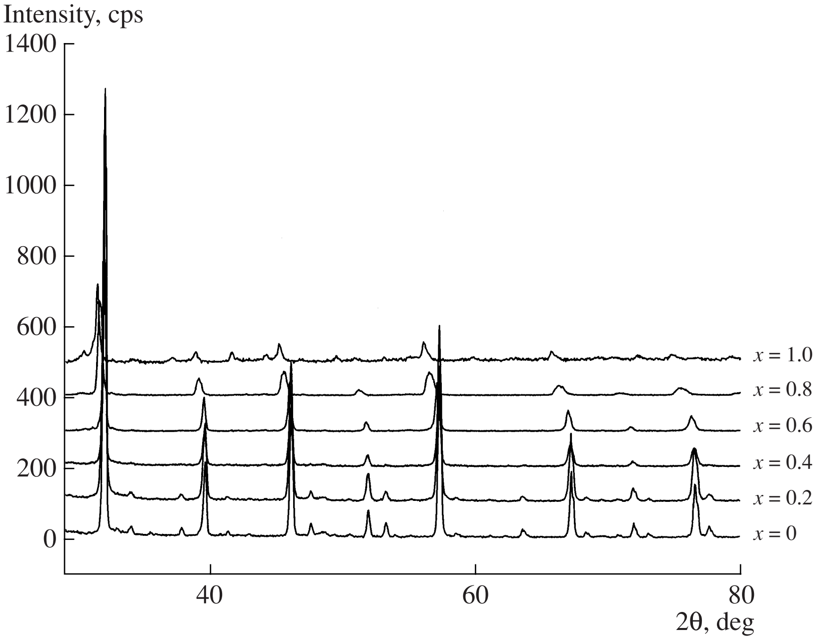

Fig. 1. X-ray diffraction patterns of $La_{1-x}Ba_xFeO_{3-\delta}$ perovskites.

EXPERIMENTAL

$La_{1-x}Ba_xFeO_{3-\delta}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1$) samples were synthesized from La_2O_3 obtained by calcination of $La(NO_3)_2$ (reagent grade) at 500°C for 4–5 h, $BaCO_3$ (reagent grade), and Fe_2O_3 (reagent grade). Mechanical treatment was performed in an APF-5 water-cooled centrifugal planetary ball mill at a centripetal acceleration of 40 g for 3 min. The ratio of the weight of the powder to be activated to the total weight of the grinding balls was 1 : 8. The activated mixture was heat-treated at 1100°C for 4 h.

X-ray powder diffraction patterns were obtained on a Bruker D8 diffractometer (Germany) using CuK_α radiation ($\lambda = 1.5418$ Å) in the 2θ scan mode (0.05° increments; counting time per point, 5 s).

Peak half-widths and integrated intensities and interplanar spacings were determined using the Eva 10.0 program, which was included in the software of the Bruker D8 spectrometer. Unit cell parameters were refined by least squares from 8–10 reflections using the Polikristall program [13].

The specific surface area (S_{BET}, m^2/g) was determined by the BET method from argon thermal desorption data.

Catalytic activity in CO oxidation was determined at 250–550°C for the 0.5–1 mm size fraction in a circulation reactor coupled with a chromatograph. The catalyst batch weight was 1 g, the circulating flow rate was 1200 l/h, and the feed (1% CO + 1% O_2 + He) flow rate was 10 l/h. The specific reaction rate at a CO concentration of 1% was calculated as

$$w, [(\text{CO molecules})\ m^{-2}\ s^{-1}] = X/(1-X)(7.47 \times 10^{17}/S_{BET}), \quad (1)$$

where X is the CO conversion. The error of the chromatographic determination of the gas component concentrations did not exceed 20%. Data reproducibility was 10% or better.

RESULTS AND DISCUSSION

According to X-ray diffraction data (Fig. 1), all the samples have a perovskite structure. A more detailed analysis has demonstrated that stoichiometric $LaFeO_3$ has an orthorhombic perovskite modification, which is in accord with our earlier publication [14]. All the $x \leq 0.2$ samples have the same structure. However, for $0.3 \leq x \leq 0.8$, the diffraction peaks characteristic of orthorhombic perovskite are missing, suggesting that the structure of the samples of these compositions is cubic. The $x = 1$ sample is a mixture of perovskite and brownmillerite. Obviously, an orthorhombic-to-cubic morphotropic phase transition (induced by compositional changes) takes place in this series of samples. (In perovskite-type solid solutions, transitions from one crystal modification to another are very frequent [15].) For ceramic $La_{1-x}Ba_xFeO_{3-\delta}$, the orthorhombic-to-cubic transition range is near $x = 0.25$ [12]. Therefore, the $x = 0.3$ sample of our series can be assigned to the region of morphotropic phase transition (RMPT).

We calculated the unit cell volume per formula unit as a function of the barium content of the sample

Table 1. Unit cell parameters of $La_{1-x}Ba_xFeO_{3-\delta}$ perovskites

x	Orthorhombic phase					Cubic phase	
	a, Å	b, Å	c, Å	$V/4$, Å^3	$(V/4)^{1/3}$, Å	a, Å	V, Å^3
0	5.563(1)	7.858(1)	5.562(1)	60.78	3.932	–	–
0.1	5.563(1)	7.860(1)	5.558(2)	60.76	3.931	–	–
0.2	5.565(2)	7.870(2)	5.563(1)	60.91	3.935	–	–
0.3	–	–	–	–	–	3.9360(5)	60.98
0.4	–	–	–	–	–	3.9376(3)	61.05
0.6	–	–	–	–	–	3.9441(3)	61.35
0.8	–	–	–	–	–	3.9770(6)	62.90

(Table 1). For clearer analysis of experimental data for $x = 0$–0.2, we use the unit cell parameter $\sqrt[3]{V}$. On passing to $x = 0.4$, the parameter $V(V/4)$ does not increase; however, on passing to the samples richer in barium, this parameter increases dramatically. Although no barium-induced changes in this parameter were detected for small x values, the weakening of the diffraction peaks characteristic of the orthorhombic phase is evidence that barium is incorporated in the perovskite structure.

In the heterovalent substitution of Ba^{2+}, a larger cation, for La^{3+} in $La_{1-x}Ba_xFeO_{3-\delta}$, the electroneutrality of the sample can be maintained via the formation of either oxygen vacancies or iron ions in higher oxidation states. The larger size of the Ba^{2+} cation, the oxygen vacancies, and the increased charge on the iron ions are the main causes of the structural changes. It is, therefore, not impossible that the main mechanism of electroneutrality conservation for the orthorhombic samples ($x < 0.3$) is the formation of Fe^{4+} cations (which are smaller than Fe^{3+}) and this is why the unit cell parameter is independent of x. For the cubic samples, the increase in the unit cell parameter observed for $x > 0.4$ possibly indicates the formation of solid solutions containing oxygen vacancies.

These data are in good agreement with the data available for the ceramic series except for $x = 0.8$ [12]. For $x = 0.6$, the unit cell parameters of the samples obtained by mechanochemical technology and ceramic processing coincide within the experimental error.

The difference between our series of samples and the ceramic series [12] is that, in the former, there is no two-phase region for the $x = 0.8$ sample and the unit cell parameter of this sample is larger than that of the single-phase ceramic sample $La_{0.33}Ba_{0.66}FeO_{3-\delta}$. This is evidence that the solid solution is richer in barium than the $x = 0.66$ sample. In view of the fact that the data presented in [12] refer to equilibrium synthesis conditions, the $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ phase examined here should be considered to be metastable. Note also the asymmetry of the diffraction peaks for $x = 0.8$: the decline of intensity is more gentle on the large-2θ side of the peaks. This may be due to the existence of a mechanochemical synthesis–induced barium concentration gradient in the particles of this sample.

The BET specific surface area of the mechanochemically synthesized samples ranges between 1 and 5 m^2/g (Table 2). According to microscopy data, the particle size is 0.5–2 μm. Therefore, the observed broadening of diffraction lines can arise either from the microdomain structure of the particles or from microstresses in the particles. A Williamson–Hall analysis [16] of the diffraction peak broadening demonstrated that the particles consist of stressed microdomains. For example, for $x = 0.4$, the size of a coherent-scattering domain (CSD) is ~400 Å and the microdistortion value is small ($\varepsilon = 0.001$). At the same time, for $x = 0.8$, the peak broadening is mainly caused by structure microdistortions ($\varepsilon = 0.004$ at a CSD size of ~700 Å). Therefore, the $La_{1-x}Ba_xFeO_{3-\delta}$ samples typically have a microdomain structure and the smaller microdomains have fewer microdistortions than the larger microdomains. It is not impossible that, in the morphotropic transition region, the microstresses are "discharged" onto interfaces and this is why the microdomains have a smaller size there. A similar situation was observed for $La_{1-x}Sr_xCoO_{3-\delta}$ materials [17, 18], including ceramic ones [18].

Table 2. Specific surface areas of $La_{1-x}Ba_xFeO_{3-\delta}$ perovskites

x	S_{BET}, m^2/g
0	1.2
0.1	4.0
0.2	5.0
0.3	3.8
0.4	3.2
0.6	2.3
0.8	1.0
1.0	1.0

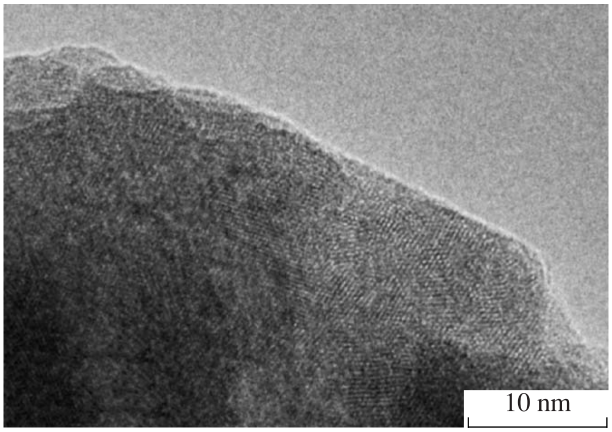

Fig. 2. Microstructure of $La_{0.4}Ba_{0.6}FeO_{3-\delta}$.

High-resolution transmission electron microscopy data confirm the existence of the microdomain structure. By way of example, Fig. 2 shows a micrograph of the $x = 0.4$ sample.

The study of the catalytic properties of the perovskite series $La_{1-x}Ba_xFeO_{3-\delta}$ in CO oxidation revealed that the specific catalytic activity depends nonmonotonically on the barium content of the sample (Fig. 3). Furthermore, the particular form of this nonmonotonic dependence depends on the catalytic test temperature. The observed differences between the catalytic activities of the samples far exceed the measurement error.

At low test temperature, catalytic activity depends only slightly on the sample composition; however, weak activity maxima can still be noticed at $x = 0.1$, 0.3, and 0.8. As the test temperature is raised to 450–550°C, the activity of the $x = 0$, 0.3, and 0.8 samples increases most greatly and the peaks at $x = 0.3$ and 0.8 clearly reveal themselves. The higher temperature activity-vs.-composition curves indicate two distinct composition ranges, namely, $x \leq 0.2$ (orthorhombic perovskite range), where the catalytic activity decreases with increasing barium content, and $x \geq 0.4$ (cubic perovskite range), where the catalytic activity increases with increasing barium content. The highest activity is shown by the $x = 0.3$ sample, whose composition corresponds to the morphotropic phase boundary. The finding that the catalytic activity increases with increasing barium content in the cubic perovskite composition range can be due to the increasing vacancy concentration and, as a consequence, the formation of extra coordinatively unsaturated active sites on the surface and an increase in the mobility of lattice oxygen. The formation of the vacancy-ordered phase brownmillerite at $x = 1$ causes a natural decrease in catalytic activity because of the decrease in the vacancy concentration. The inverse composition dependence in the range of orthorhombic solutions can then be explained by assuming either the absence of vacancies in the samples (the unit cell parameter is invariable) or barium segregation on the surface, which can cause the formation of tightly bound carbonate ions and the blocking of part of the active sites. As in the case of the La–Sr–Co(Fe)–O systems, the sample from the morphotropic transition region is the most active. It is possible that the high activity of this sample is due to high oxygen mobility along interdomain/interphase boundaries, which was observed earlier in calcium-substituted materials [2, 14]. Furthermore, the test temperatures of 500–550°C possibly give rise to a polymorphic transition during which the lattice oxygen is loosely bound and highly mobile.

The comparatively large increase in the catalytic activity observed for the $x = 0$ sample as the test temperature is raised can be due to the formation of a rather stable vacancy-containing phase in this phase, as was reported in our earlier publication [19].

Thus, this catalytic study has demonstrated that the specific catalytic activity of the system depends on the sample composition and test temperature in a complicated way. Raising the test temperature can cause changes in the ratio of point and extended defects. Further investigation is required to elucidate this point.

It has been demonstrated here that the perovskites can readily be synthesized from mechanically activated mixtures of their constituent oxides. A specific feature of the perovskite series examined here is the formation of the metastable phase $La_{0.2}Ba_{0.8}FeO_{3-\delta}$. This metasta-

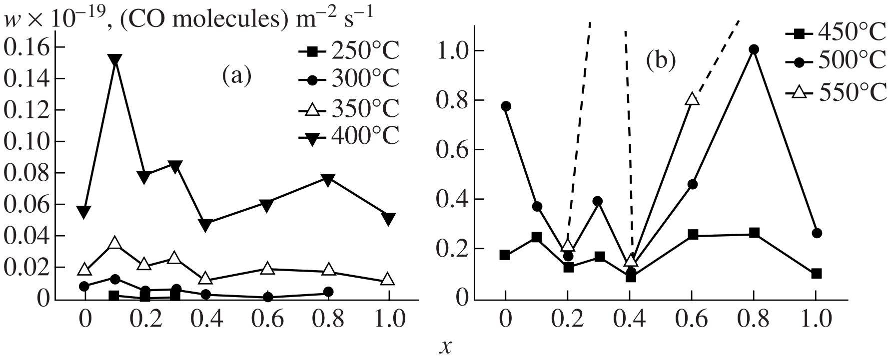

Fig. 3. CO oxidation rate as a function of the catalyst composition at (a) low and (b) high catalytic test temperatures.

ble phase and a sample from the RMPT ($La_{0.7}Ba_{0.3}FeO_{3-\delta}$) show a comparatively high catalytic activity in carbon monoxide oxidation.

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