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Mechanochemical synthesis and reactivity of $La_{1-x}Sr_xFeO_{3-y}$ perovskites ($0 \leq x \leq 1$)

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Mechanochemical synthesis of $La_{1-x}Sr_xFe_{3-y}$ ($0 \leq x \leq 1$) perovskites was carried out from simple oxides. Undoped lanthanum ferrite samples calcined at 900 and 1100°C for 4 h are nearly single-phase systems, while some substituted ones (samples with $0.3 \leq x \leq 0.8$ calcined at 900°C and samples with $x = 0.3$, $x = 0.4$ and $x = 0.8$ calcined at 1100°C) are two-phase systems consisting of orthorhombic perovskite $La_{1-x}Sr_xFeO_{3-y}$ (A) and cubic or tetragonal perovskite $Sr_zLa_{1-z}FeO_{3-y}$ (B) phases. In CO and CH_4 oxidation processes, the specific catalytic activity (SCA) of samples calcined at 1100°C varies non-monotonously with the Sr content. In CO oxidation, SCA reaches a maximum in the range of La substitution by Sr where phase transition occurs and samples are comprised of two coexisting phases ($x = 0.3$ and 0.8). In CH_4 oxidation, SCA decreases with the Sr content.

1. Introduction

Recently, substituted perovskites $La_{1-x}Sr_xMO_{3-y}$ (M = 3d elements) have attracted much attention because of their high electronic/ionic conductivity and good catalytic performance in deep oxidation processes [1, 2]. Besides, perovskite-type oxides are applied as chemical sensors, electrodes in high temperature fuel cells etc. [3]. This requires development of new inexpensive and wasteless methods of dispersed perovskites synthesis. Mechanochemical activation of the mixture of solid reagents followed by annealing in mild conditions (MA route) was recently shown to meet such demands [4]. Since the phase/surface composition and real (defect) structure of complex perovskites are known to depend on the preparation route [5–7], detailed investigation of the properties of $La_{1-x}Sr_xFeO_{3-y}$ system prepared by the MA route was carried out in this study.

2. Experimental

$La_{1-x}Sr_xFeO_{3-y}$ samples were prepared from simple oxides ('chem. pure' La_2O_3, $SrCO_3$, Fe_2O_3) by using preliminary mechanical treatment (MT) of the stoichiometric mixture of starting compounds in the high-energy planetary ball mills APF-5 [8]. The ratio of the weights of milling balls and oxides powder was equal to 10:1, acceleration (achieved in the drums of the mills) ~40 g. MT time was 3 min. After MT procedure, the powders were annealed at 900 or 1100°C for 4 h on air.

XRD patterns were obtained with a URD-6 diffractometer (Germany) using Cu-K_α radiation ($\lambda = 1.5418$ Å). The scanning region 2θ was equal to 20–90° with step = 0.05°. The experimental data analysis was carried out by APX-63 and ORIGIN-6.0 programs. Precise estimation of the unit cell parameters were carried out by the least-squares method (Program "Polycrystall" [9]) using 8–10 diffraction peaks. The particle sizes and microstrain densities were calculated by the approximation method using Williamson-Hall [10].

The specific surface area (S_{sp}, m^2/g) was determined by the BET method using Ar thermal desorbtion data.

The method of the differential phase dissolving (MDPD) was used to determine the phase composition (including amorphous phases, phases in amount <5%) and to analyse the cation ratio in the synthesis products [11]. Samples were dissolved in hydrochloric acid solution with concentration ranging from 1 to 10 N, while the temperature was increased from 20 to 100°C, solution analysis being carried out with the help of the atomic absorption spectroscopy (a BAIRD spectrometer).

The specific catalytic activity (SCA) in the CO oxidation process was determined at 300–500°C in the batch-flow installation equipped with the gas chromatographic analysis of reaction mixture components. Sample weight was 1 g, particle size was 0.5–1 mm, gas circulation velocity was 1200 l/h, feed rate (1% CO + 1% O_2 in He) was 10 l/h. Before the activity measurements, samples were pretreated in the O_2 flow at 400°C for 2 h.

The SCA in the reaction of CH_4 oxidation was determined at 350–600°C for samples with the particle

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size 0.5–1 mm and weight 1 g in the flow installation equipped with the gas chromatographic analysis. The reaction mixture (0.5% CH_4 + 9% O_2 in He) feed rate was 2.4 l/h.

3. Results and discussion

3.1. Phase composition

Time and temperature of calcination were found to be one of the main factors determining the phase composition of samples. Here the effect of the calcination temperature will be considered for the samples prepared by MA route.

For pure lanthanum ferrite and strontium ferrite systems, MT permits to substantially decrease the time of synthesis. So, according to MDPD and XRD data, the samples with compositions $x = 0$ and $x = 1$ calcined at 900 and 1100°C are nearly single-phase systems consisting of orthorhombic perovskite $LaFeO_3$ and tetragonal perovskite $SrFeO_{3-y}$, with the amount of product around 81–83% and 92–98%, respectively (Table I, Fig. 1).

According to XRD data (Fig. 2a), samples with $x = 0.3$–0.7 calcined at 900°C consist of two perovskite-like phases: orthorhombic perovskite $La_{1-x}Sr_xFeO_{3-y}$ (A) and cubic perovskite $Sr_zLa_{1-z}FeO_{3-y}$ (B) phases. Similarly, in samples with $x = 0.3$–0.8, MPDD experiments also revealed the presence of two perovskite phases (differing by the Sr content, Table I).

After calcination at 1100°C, as judged by XRD data (Fig. 1, Fig. 2b), only samples with $x = 0.3$ and $x = 0.4$ are comprised from A and B phases. The same feature was revealed by MDPD for the sample with $x = 0.8$ as well. Hence, the specificity of the MT synthesis route is in the formation of two-phase samples, while other preparation methods (ceramic [12], auto-combustion [13], alkaline coprecipitation [14]) are reported to give single-phase solid solutions $La_{1-x}Sr_xFeO_{3-y}$ for all composition range $0 < x < 1$. However, it is to be noted that a detailed investigation [15] of $La_{1-x}Sr_xFeO_{3-y}$ system prepared by ceramic route also revealed the complex phase composition of samples with $x = 0.3$, 0.4, 0.8, 0.9, 1.0 depending on the conditions of synthesis (calcination temperature, oxygen pressure, quenching regimes etc.).

The analysis of the unit cell parameters dependence on the calcination temperature revealed that the phase A is a solid solution with the variable composition (Fig. 2). The solubility of Sr in this phase calcined at 900°C reaches the saturation for $x = 0.6$ and 0.7, while for samples calcined at 1100°C this occurs at $x = 0.4$. The cell parameter of the phase A is practically independent upon the calcination temperature, while that of the phase B varies with the temperature (Fig. 2a). In order to precise the unit cell parameter of A and B phases additional annealing at $T = 1200$°C for 10 h of the samples $La_{1-x}Sr_xFeO_{3-y}$ calcined at 1100°C was carried out. It is to be noted that cell parameters for phase

TABLE I Overall cation stoichiometry, phase composition and stoichiometry of $La_{1-x}Sr_xFeO_{3-y}$ samples according to MDPD data

Sample nominal composition (S_{sp}, m^2/g calcined at 1100°C)	Total cation stoichiometry in the samples	Phase composition (cation ratio) for samples calcined at 900°C	Phase composition (cation ratio) for samples calcined at 1100°C
$LaFeO_3$	$La_{0.97}Fe_1$	La_1Fe_1—82.5	$La_{0.94}Fe_1$—98.1
(1.4)		Fe—0.5	Fe—0.8
		La—17.0	La—1.1
$La_{0.8}Sr_{0.2}FeO_{2.9}$	$La_{0.78}Sr_{0.22}Fe_1$	$La_{0.82}Sr_{0.1}Fe_1$—95*	$La_{0.75}Sr_{0.13}Fe_1$—90.6
(3.1)		Fe—0.2	Fe—6.8
		La—3.3	Sr—2.1
$La_{0.7}Sr_{0.3}FeO_{2.85}$	$La_{0.68}Sr_{0.32}Fe_1$	$La_{0.81}Sr_{0.14}Fe_1$—86.4*	$La_{0.75}Sr_{0.13}Fe_1$—82.0
(2.6)		Sr_1Fe_1—6.5	Sr_1Fe_1—9.0
		Fe—0.1	Fe—8.1
		La—1.4	La—0.1
		Sr—5.6	Sr—0.8
$La_{0.6}Sr_{0.4}FeO_{2.8}$	$La_{0.57}Sr_{0.39}Fe_1$	$La_{0.75}Sr_{0.13}Fe_1$—78	$La_{0.95}Fe_1$—11.8
(1.8)		Sr_1Fe_1—17.1	$La_{0.58}Sr_{0.48}Fe_1$—85.1
		La—0.9	Fe—0.9
		Sr—3.0	Sr—1.8
$La_{0.4}Sr_{0.6}FeO_{2.7}$	$La_{0.39}Sr_{0.55}Fe_1$	$La_{0.52}Sr_{0.14}Fe_1$—69.7*	
(1.3)		Sr_1Fe_1—17.6	$La_{0.42}Sr_{0.51}Fe_1$—95.9
		Fe—1.2	Fe—1.1
		La—1.0	La—0.5
		Sr—10.5	Sr—2.5
$La_{0.3}Sr_{0.7}FeO_{2.65}$	$La_{0.29}Sr_{0.66}Fe_1$	$La_{0.32}Sr_{0.25}Fe_1$—68.3	
(0.5)		Sr_1Fe_1—16.2	$La_{0.31}Sr_{0.65}Fe_1$—95.4
		Fe—1.0	Fe—1.5
		La—3.4	La—2.1
		Sr—11.1	Sr—1.0
$La_{0.2}Sr_{0.8}FeO_{2.6}$	$La_{0.20}Sr_{0.75}Fe_1$	$La_{0.32}Sr_{0.25}Fe_1$—47.7	$La_{0.23}Sr_{0.76}Fe_1$—83
(0.9)		Sr_1Fe_1—38	Sr_1Fe_1—13.2
		Fe—4,4	Fe—5.9
		Sr—9.8	Sr—2.3
$SrFeO_{3-x}$	$Sr_{0.9}Fe_1$	SrFe—81.5	$Sr_{0.9}Fe_1$—92.2
(0.1)		Fe—12.8	Fe—3.8
		Sr—4.9	Sr—3.3

*Composites with variable surface/bulk composition.

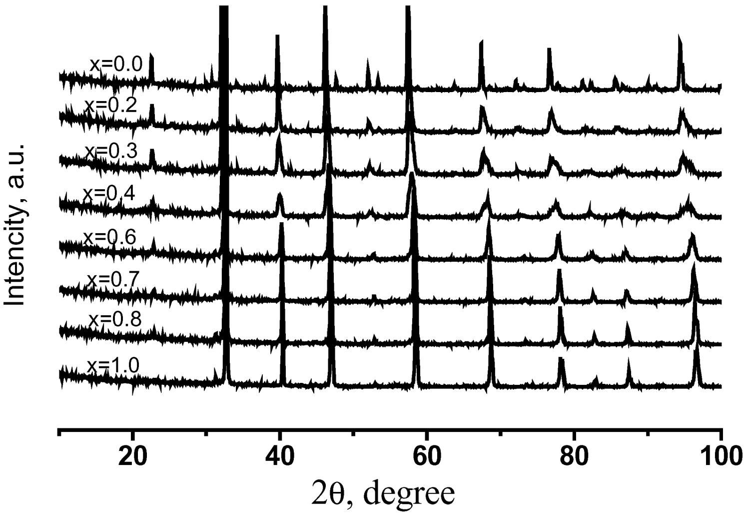

Figure 1 X-ray diffraction patterns of $La_{1-x}Sr_xFeO_{3-y}$ samples calcined at 1100°C for 4 h.

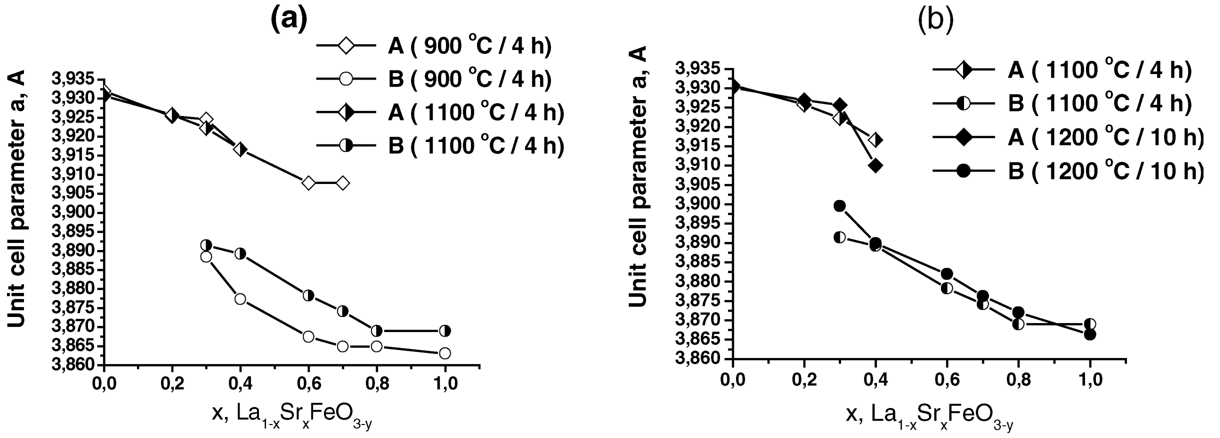

Figure 2 The lattice parameter a (in Å) of $La_{1-x}Sr_xFeO_{3-y}$ samples versus Sr content (x); (a) - samples calcined at 900 and 1100°C; (b) - Samples calcined at 1100 and 1200°C.

A and B continue to change even for samples calcined at 1200°C (Fig. 2b), especially for $x = 0.3$ (phase A) and $x = 0.4$ (phase B). Since parameter variations were most noticeable for the samples $x = 0.3$ and $x = 0.4$, morphotropic phase transition could be suggested at the region $x = 0.3$–0.4, and its appearance could cause the formation of the specific microstructure of samples (microheterogeneity, for instance).

In order to determine the samples microstructural parameters, the broadening of the XRD peaks was thoroughly studied. The narrow X-ray diffraction peaks of samples with $x = 0$ and $x = 1$ imply that they are comprised of big well crystallized particles free of microstrains with typical sizes exceeding 1500 Å. For intermediate samples of the $La_{1-x}Sr_xFeO_{3-y}$ system calcined at 900 and 1100°C, the prominent broadening of the XRD peaks was observed, but correct estimation of particle sizes for two-phase samples is complicated by overlapping of peaks corresponding to A and B phases. Hence, particle sizes (D) and microstrains density ($\Delta d/d$) were calculated only for single-phase samples with $x = 0.6$ and $x = 0.7$ calcined at 1100 and 1200°C (Table II). These data imply that for the phase based upon strontium ferrite, the increase in the La content generates microstrains and decreases particle sizes. The absence of prominent difference in those parameters between samples calcined at 1100 and 1200°C indicates that microstrains are not the consequence of the MT but appear due to differences in Sr/La ionic radii, presence of oxygen vacancies and/or samples chemical inhomogeneity. As follows from Table II, the instability of phase B (proportional to the microstrains density $\Delta d/d$) increases with the La content, and appearance of the second phase (A) could be accompanied by development of the samples microheterogeneity.

The microheterogeneity of samples could be proposed from the MDPD data. Analysis of the MDPD stoichiograms suggests a complex morphological structure of those samples particles, namely, formation of composites (marked as '*' in the Table I). Thus, for the

TABLE II Particle size (D) and microstrains density ($\Delta d/d$) for phase B

	Calcination temperature (°C)			
	1100		1200	
Composition	D (Å)	$\langle \Delta d/d \rangle$	D (Å)	$\langle \Delta d/d \rangle$
0.6	630	0.0013	630	0.0014
0.7	1400	0.001	1000	0.0011

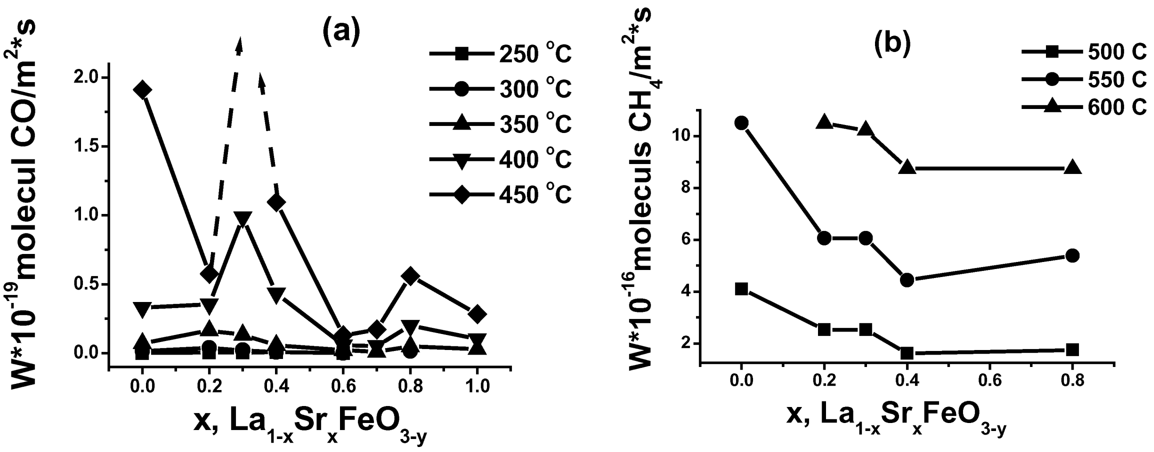

Figure 3 Specific catalytic activity versus x for mechanically treated $La_{1-x}Sr_xFeO_{3-y}$ samples annealed at 1100°C. Test temperature 250–600°C. (a) - CO catalytic oxidation, (b) - CH_4 catalytic oxidation.

sample with $x = 0.2$ calcined at 900°C, the surface layer of particles corresponds to $La_{0.82}Sr_{0.28}FeO_{3-y}$ composition, while the bulk one—to $La_{0.82}Sr_{0.1}FeO_{3-y}$ (Table I). These data indicate that the surface is enriched by Sr and depleted with La cations. A similar enrichment of the surface layer of doped lanthanum manganite or cobaltite prepared by MA route by alkaline-earth cations was earlier described in our works [16, 17]. This effect seems to be typical for substituted perovskites prepared via MA route and implies two-component composites formation at the MT stage. Probable microheterogeneity in the range of $La_{1-x}Sr_xFeO_{3-y}$ samples certainly requires further studies.

3.2. Catalytic activity

For $La_{1-x}Sr_xFeO_{3-y}$ samples calcined at 1100°C, the specific catalytic activity in CO oxidation changes non-monotonously versus x, especially for high reaction temperatures (Fig. 3a). There are two maxima of SCA at $x = 0.3$ and $x = 0.8$. So, SCA reaches a maximum in the range of La substitution by Sr where the phase transition occurs and samples are comprised of two coexisting phases (at $x = 0.3$ and $x = 0.8$), where a presence of microheterogeneity could be proposed. The activity maxima could be assigned to the development of the high density of the interphase/intergrain boundaries.

In CH_4 oxidation process, the Sr-substitution in $LaFeO_3$ leads to decreasing of SCA (Fig. 3b), all substituted samples show a similar SCA with CO_2 selectivity of 100%. Though any apparent maximum in the dependence of activity versus x is not observed, there is some curve inflection in the range corresponding to the phase transition as well. Much weaker effect of the real structure of samples on the specific activity in methane catalytic oxidation can be assigned either to a higher temperature of experiments (hence, less pronounced role of weakly bound oxygen stabilized on defect centers), or by the surface hydroxylation known to occur easily for those Sr-containing systems under contact with water, which rearranges the surface layer decreasing the amount of active centers—coordinatively unsaturated surface cations.

Hence, catalytic activity of $La_{1-x}Sr_xFeO_{3-y}$ samples in CO and CH_4 oxidation changes non-monotonously with the Sr content. The difference in activity of $LaFeO_3$ and its Sr-substituted derivatives is increased with an increase of the temperature of the activity tests. Though in general the activity of Sr-substituted samples is lower as compared with pure lanthanum ferrite, some doped samples display a higher or close level of activity. This difference in activities is more noticeable in CO oxidation and less in CH_4 oxidation. Since the samples with $x = 0.3$ and $x = 0.8$ are two-phase systems, their enhanced activity can be tentatively explained by the specificity of the microstructure, which certainly requires further studies.

4. Conclusion

The phase composition of $La_{1-x}Sr_xFeO_{3-y}$ samples prepared via MA route strongly depends upon the temperature and time of calcination of the activated mixture. For samples calcined at 900°C there is a broad two-phase region at x within 0.3–0.8 range. For samples calcined at 1100°C only those with $x = 0.3$, 0.4 and 0.8 are two-phase systems, which agrees with earlier obtained results of Dann *et al.* [15] for $La_{1-x}Sr_xFeO_{3-y}$ system prepared by ceramic method. Hence, the complex phase composition of the $La_{1-x}Sr_xFeO_{3-y}$ system seems to be caused not by the samples preparation technology but by the dopant content. Catalytic activity of the $La_{1-x}Sr_xFeO_{3-y}$ perovskites prepared via MA route in the reactions of CO and methane oxidations appears to be determined both by the samples microstructure and the surface layer modification under the reaction media effect.

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