

Conduction and Ion Transport in LaYO₃ Doped with CaO

V. B. Balakireva^z, A. Yu. Stroeva, and V. P. Gorelov

*Institute of High-Temperature Electrochemistry, Ural Division, Russian Academy of Sciences,
ul. S. Kovalevskoi 20, Yekaterinburg, 620219 Russia*

Received June 16, 2004

Abstract—Values of partial conductions (ionic: protonic, oxygen, hole) and their activation energies in LaYO₃ are determined at 700–1050°C, p_{O_2} ranging from air to 10^{-15} Pa, and $p_{\text{H}_2\text{O}} = 0.04$ –13.5 kPa for different versions of doping with calcium (when introduced into the lanthanum or yttrium sublattices, or into both sublattices simultaneously). The conductivity increases in the series $\text{La}_{0.97}\text{Ca}_{0.03}\text{YO}_{3-\alpha} < \text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha} < \text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, which means that the stoichiometric composition with a 1 : 1 ratio between Y and La has the highest conductivity.

Key words: perovskites, LaYO₃, ion transport numbers, proton conduction, hole conduction

INTRODUCTION

Great attention is paid nowadays to studying high-temperature proton transport in oxides with a perovskite structure, which demonstrate the highest proton conductivity [1–4]. The interest aroused by these materials is due to the possibility of using them as proton-conducting solid electrolytes in medium- and high-temperature electrochemical devices, such as fuel cells, electrolyzers for hydrogen production, and hydrogen sensors.

Equimolar compounds of rare earth oxides $\text{Ln}'\text{LnO}_3$ where Ln' and Ln are lanthanides with the oxidation degree 3+ are also classified with compounds of a perovskite structure. An acceptor doping of $\text{Ln}'\text{LnO}_3$ gives rise to ionic conduction, which is of a mixed (proton–oxygen) nature in humid atmosphere [5–9]. An obvious application advantage of these materials is their higher chemical resistance as compared to the well known SrCeO_3 - and BaCeO_3 -based proton-conducting solid electrolytes.

A well known example of such compounds is LaYO₃, whose structure was studied in [10]; it is an ordered phase of a perovskite type, rather than perovskite proper, with parameters of its monoclinic cell $a = 1.6925$ nm, $b = 1.6866$ nm, $c = 1.6870$ nm, and $\beta = 92.01^\circ$. This phase may be called pseudocubic. An order \rightleftharpoons disorder phase transition occurs in it at $1505 \pm 20^\circ\text{C}$ [10]. Recently it has been confirmed yet once again [11] that the high-temperature, i.e. disordered, phase of LaYO₃ has a monoclinic structure of the Sm_2O_3 type.

Of late properties of twice-doped perovskites, i.e. upon adding dopants simultaneously to both sublattices, were extensively studied.

Here we evaluate the conductivity and the ion and proton transport numbers of CaO-doped LaYO₃ at different doping modes with calcium (lanthanum sublattice, yttrium sublattice, or both) and as a function of the La : Y ratio in LaYO₃.

EXPERIMENTAL

The samples were synthesized by a ceramic technology from raw materials LaO_{1.5} (99.94%), YO_{1.5} (99.87%), and CaCO₃ (analytical grade). Weights of reagents were mixed in a jasper mortar in ethanol. The mixtures were calcined at 900°C; then sample bars, 17 by 4 by 4 mm, were pressed at 200 MPa for the conductivity measurements and rings of 14 mm in diameter, for the transport number measurements. The pressed samples were fired in air at 1550°C for 3 h. The density of the ceramic thus prepared was 84–95.5% of the theoretical. The silicon content was less than 0.02 wt % (element analysis, Jobin Yvon 48). An x-ray diffraction analysis was performed using a DRON-3-IBM PC/AT instrument, with filtered CuK_α radiation.

The samples' conductivity was measured by a two-probe method, using a bridge circuit with a rectangular pulse generator. The pulse repetition frequency was 70 kHz. This circuit allowed us to compensate (by watching the oscilloscope's screen) only the active component of the cell's resistance. For the sample geometry ($l/s \approx 12$ 1/cm), this procedure practically eliminated the effect of electrodes. The accuracy of the

^z Corresponding author, e-mail: v.balakireva@ihte.uran.ru

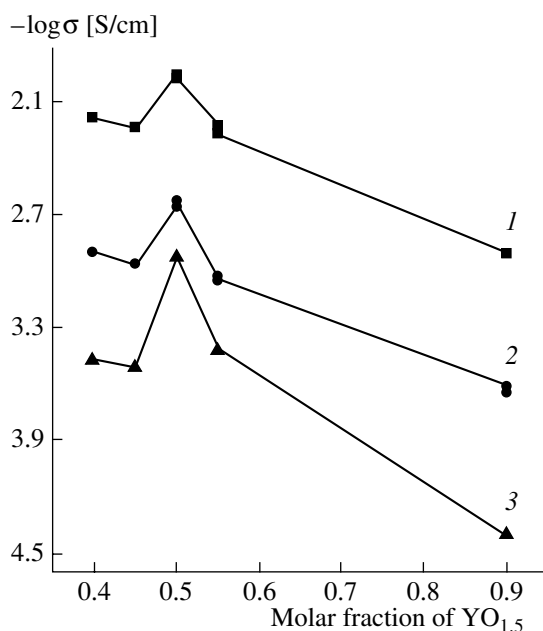


Fig. 1. Net conductivity in (1) air and (2) reductive atmosphere at $p_{O_2} = 10^{-15}$ Pa, and (3) protonic conductivity in air at 1000°C for $0.995[(1-x)\text{YO}_{1.5} + x\text{LaO}_{1.5}] + 0.005\text{CaO}$.

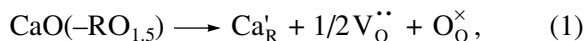
bridge measurements was 5–0.5%, depending on the resistance value.

Platinum powder electrodes were painted onto the samples and then fired at 1000°C for one hour. The electroconductivity was measured at $700\text{--}1010^\circ\text{C}$ in the p_{O_2} range from air to 10^{-15} Pa and $p_{H_2O} = 0.04\text{--}13.5$ kPa. The activation energies for conduction were determined from slopes of the temperature dependences of the conductivity ($\log \sigma T$ vs. $1/T$).

The overall transport number for ions t_i and that for protons t_H were determined by an emf method, using oxygen and water-vapor concentration cells. Different oxygen partial pressures at either side of a sample were set up using electrochemical pumps and monitored by electrochemical sensors made of a ZrO_2 -based electrolyte. Partial pressures of water vapor were set up by bubbling gas through water of a specified temperature or by passing through a zeolite-packed column. The procedure is described at length in [12, 13].

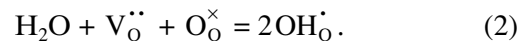
RESULTS AND DISCUSSION

Doping LaYO_3 with CaO generates substitutional defects Ca'_R and oxygen vacancies $V_O^{\bullet\bullet}$ in the quasi-chemical reaction (Kroeger–Wink notation)

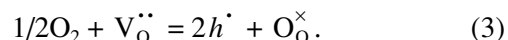


where $R = \text{La}$ or Y . The oxygen vacancies in an oxide facilitate oxygen migration at higher temperatures and

can interact with water vapor, yielding protons OH'_O , hence protonic conduction (protons are localized on oxygen ions)



In oxidative atmospheres, the interaction of oxygen vacancies with oxygen of the gas phase generates holes h^\cdot and gives rise to hole conduction



Then, from the mass-action law for (3), the hole concentration p is

$$p = [h^\cdot] = K[V_O^{\bullet\bullet}]^{1/2}p_{O_2}^{1/4}. \quad (4)$$

The effect of the $\text{La} : \text{Y}$ ratio on the conductivity of doped LaYO_3 was studied for $0.995[(1-x)\text{YO}_{1.5} + x\text{LaO}_{1.5}] + 0.005\text{CaO}$ ($x = 0.1\text{--}0.6$). The maximal conductivity (including protonic conductivity) was observed for the stoichiometric composition in which this ratio is 1 : 1. Any deviation from this composition drastically decreases the conductivity (Fig. 1) and leads to a disordering of LaYO_3 and to a decrease in conductivity. A similar effect was observed in LaYO_3 upon exceeding the disordering temperature [10].

To evaluate the effect of different modes of doping with calcium (to the lanthanum sublattice, yttrium sublattice, or both sublattices simultaneously) on the LaYO_3 conductivity, we synthesized compositions $\text{La}_{0.97}\text{Ca}_{0.03}\text{YO}_{3-\alpha}$, $\text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, and $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$ and examined their conductivity. Their density was 95.5% of the theoretical. The temperature dependences of the net and ionic conductivity in air and a reductive atmosphere were linear in the Arrhenius coordinates. The conductivity increased (Fig. 2a) in the above series. Again the stoichiometric composition with the $\text{Y} : \text{La}$ ratio equal to 1 : 1 had maximal conductivity and minimal activation energy for conduction ε (for ionic conduction, $\varepsilon = 51.7 \pm 0.2$ kJ/mol). Samples with nonstoichiometric $\text{Y} : \text{La}$ ratios of 0.97 : 1 and 1 : 0.97 had identical and noticeably higher activation energies (for ionic conduction, $\varepsilon = 66.7 \pm 0.2$ kJ/mol). For the other samples, the conductivities measured in air and a reductive atmosphere are given in Fig. 2b.

The conductivity of all compositions studied depended similarly on p_{O_2} : it decreased with decreasing p_{O_2} . At lower pressures the dependence had a horizontal segment of practically ionic conduction σ_i ; see data for $0.995(0.5\text{YO}_{1.5} + 0.5\text{LaO}_{1.5}) + 0.005\text{CaO}$ in Fig. 3a. At lower temperatures the horizontal segment was longer. Such dependences of the net conductivity σ_{net} on p_{O_2} are characteristic of mixed ion–hole semiconductors: the hole conductance, which dominates in air, decreases with decreasing p_{O_2} . We determined the hole conductivity as follows: $\sigma_p = \sigma_{\text{net}} - \sigma_i$; it depended on p_{O_2} to the power of 1/4 (Fig. 3b), in agreement with (4).

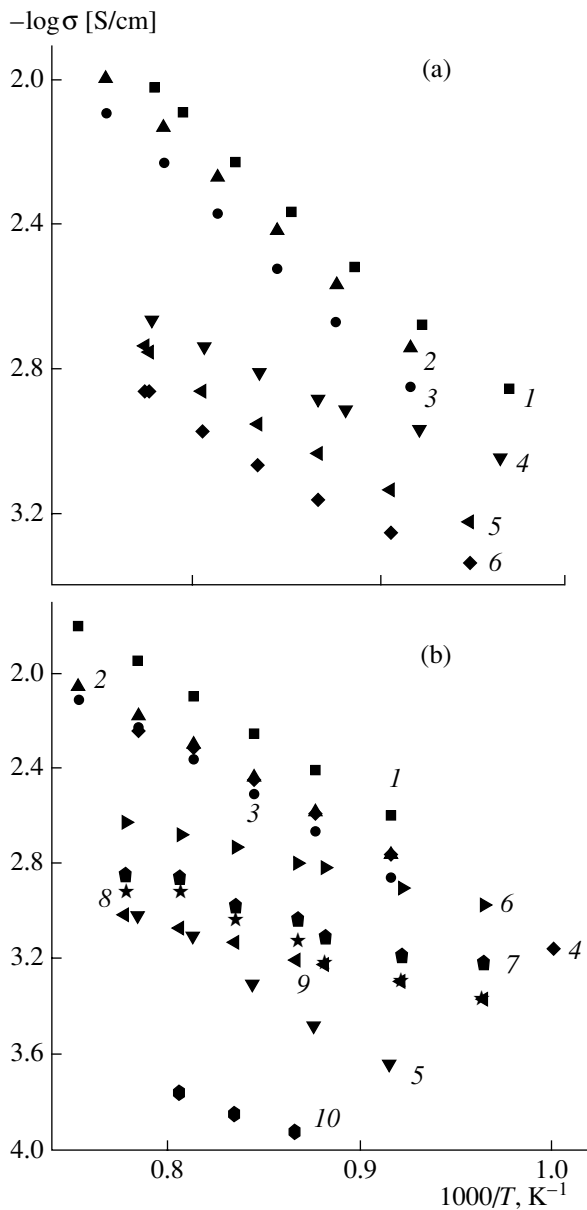


Fig. 2. Temperature dependences of net conductivity (a) in (1–3) air and (4–6) reductive atmosphere at $pO_2 = 10^{-15}$ Pa for (1, 4) $La_{0.985}Y_{0.985}Ca_{0.03}O_{3-\alpha}$, (2, 5) $LaY_{0.97}Ca_{0.03}O_{3-\alpha}$, and (3, 6) $La_{0.97}Ca_{0.03}YO_{3-\alpha}$; and (b) in (1–5) air and (6–10) reductive atmosphere at $pO_2 = 10^{-15}$ Pa for (1, 6) $0.995(0.50YO_{1.5} + 0.50LaO_{1.5}) + 0.005CaO$, (2, 7) $0.995(0.40YO_{1.5} + 0.60LaO_{1.5}) + 0.005CaO$, (3, 8) $0.995(0.45YO_{1.5} + 0.55LaO_{1.5}) + 0.005CaO$, (4, 9) $0.995(0.55YO_{1.5} + 0.45LaO_{1.5}) + 0.005CaO$, and (5, 10) $0.995(0.90YO_{1.5} + 0.10LaO_{1.5}) + 0.005CaO$.

The shape of $\log \sigma_{net}$ vs. $\log pO_2$ curves depended on the gas humidity (Fig. 3a): the oxidation branch went steeper and the ionic horizontal, lower, with decreasing pH_2O ; i.e. the ionic and hole conductivities depend on the gas humidity.

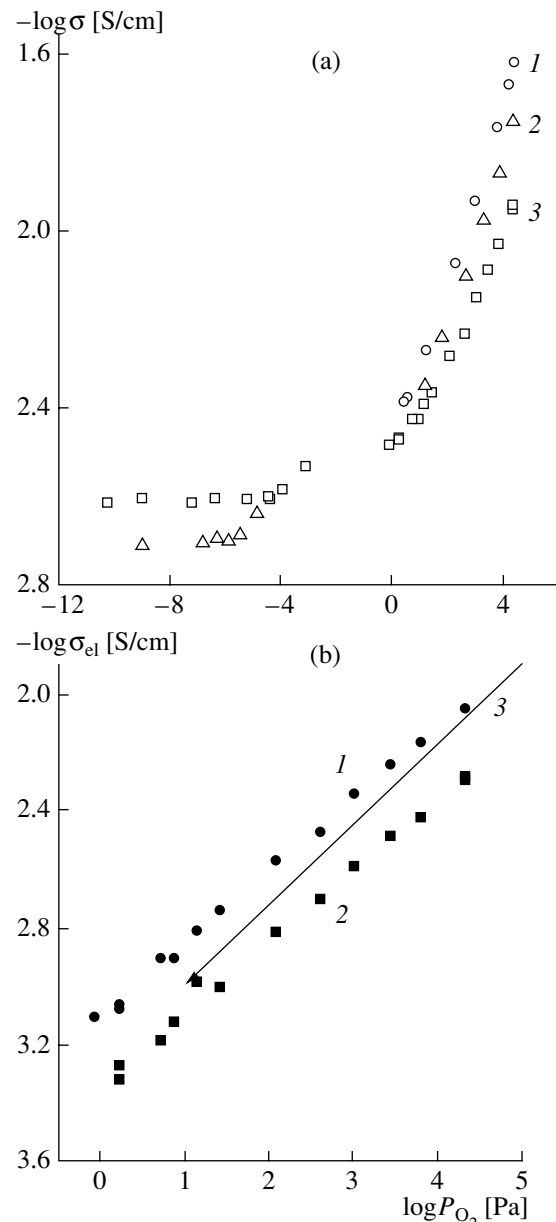


Fig. 3. Dependences on pO_2 of (a) conductivity of $0.995(0.50YO_{1.5} + 0.50LaO_{1.5}) + 0.005CaO$ at $1010^\circ C$ and pO_2 of (1) 0.04, (2) 0.37, (3) 2.34 kPa and (b) hole conductivity for (1) $0.995(0.50YO_{1.5} + 0.50LaO_{1.5}) + 0.005 CaO$ and (2) $0.995(0.55YO_{1.5} + 0.45LaO_{1.5}) + 0.005 CaO$; solid line 3 is for a slope of 1/4 at $1100^\circ C$ and $pH_2O = 2.34$ kPa.

We measured the conductivity for different compositions as a function of pH_2O in air and a reductive atmosphere ($pO_2 = 10^{-13}$ to 10^{-14} Pa) at $1010^\circ C$. In air σ_{net} (80–90%, hole conduction) varied as $\sim pH_2O^{-1/n}$, where $1/n = 6–50$ (Fig. 4). Such values of $1/n$ defy the model of oxygen vacancies, for which $1/n = 2$. Value $1/n = 6$ is realized in the model of interstitial dissolution of water vapor, as it was shown for CaO-doped $YO_{1.5}$ in [14].

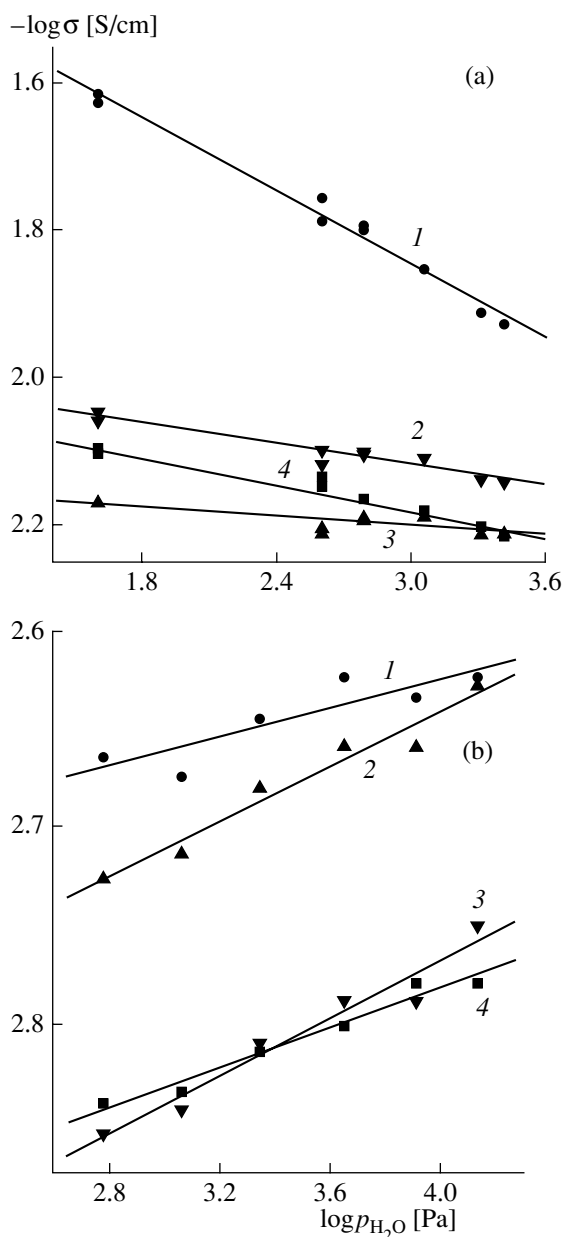


Fig. 4. Dependences of net conductivity on $p_{\text{H}_2\text{O}}$ at 1010°C for (1) $0.995(0.50\text{YO}_{1.5} + 0.50\text{LaO}_{1.5}) + 0.005\text{CaO}$, (2) $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, (3) $\text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, and (4) $0.995(0.55\text{YO}_{1.5} + 0.45\text{LaO}_{1.5}) + 0.005\text{CaO}$ in (a) air and (b) reductive atmosphere at $p_{\text{O}_2} = 10^{-13}$ to 10^{-14} Pa.

The ion and proton transport numbers increased with the air humidity (Fig. 5). The composition $0.995\text{LaYO}_3 + 0.005\text{CaO}$ had the highest part of ionic condition ($t_i = 0.64$ at 740°C). With increasing temperature, t_i decreased and at 1010°C was equal to 0.17–0.20 for all compositions other than $0.995[0.9\text{YO}_{1.5} + 0.1\text{LaO}_{1.5}] + 0.005\text{CaO}$, for which $t_i = 0.07$.

In a reductive domain, σ_{net} increased as $p_{\text{H}_2\text{O}}^{1/n}$, where $1/n = 14\text{--}30$ (Fig. 4). In this domain, in the studied temperature range, all the compositions are ionic

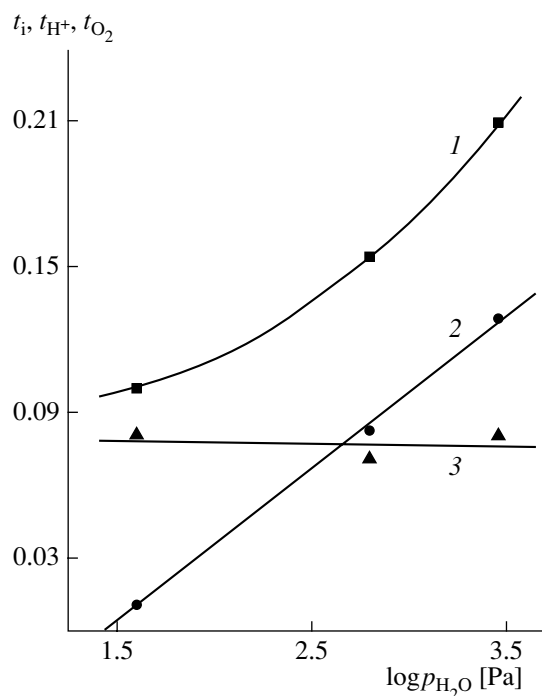


Fig. 5. Dependences of transport numbers for (1) ions, (2) protons, and (3) oxygen on $p_{\text{H}_2\text{O}}$ for $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$ in air at 915°C .

conductors with a significant part of the protonic component. According to (2), increasing $p_{\text{H}_2\text{O}}$ promotes protonic conduction.

The highest part and magnitude of protonic conductivity in air ($p_{\text{H}_2\text{O}} = 2.1$ kPa) is inherent in $0.995\text{LaYO}_3 + 0.005\text{CaO}$, for which t_{H} increased from 0.10 to 0.50 with the temperature decreased from 1000 to 740°C . For other compositions, $t_{\text{H}} = 0.32 \pm 0.01$ at 740°C . The exception is $0.995[0.9\text{YO}_{1.5} + 0.1\text{LaO}_{1.5}] + 0.005\text{CaO}$, for which the ionic-conduction part is small and varies from 0.05 to 0.2 in the 1000 to 740°C temperature range. In a reductive atmosphere, the ionic-conduction part is higher than in air, it equals 0.75–0.80 at 750°C and at 1000°C decreases to 0.70 for $0.995\text{LaYO}_3 + 0.005\text{CaO}$ and to 0.30–0.40 for other compositions.

The temperature dependences of the protonic conductivity in air and a reductive atmosphere exhibit a maximum (Fig. 6), more pronounced in the reductive atmosphere (in air it probably occurs at higher temperatures); its nature was discussed in [15]. In the reductive atmosphere the protonic conductivity is higher than in air.

The oxygen conductivity was calculated as the difference between ionic and protonic conductivities, which is valid if the ion transport is entirely performed by oxygen ions and protons. Its temperature dependences in air and a reductive atmosphere are linear in the Arrhenius coordinates (Fig. 7). It is practically independent of the atmosphere composition. The highest part and magnitude of the oxygen-ion conductivity is

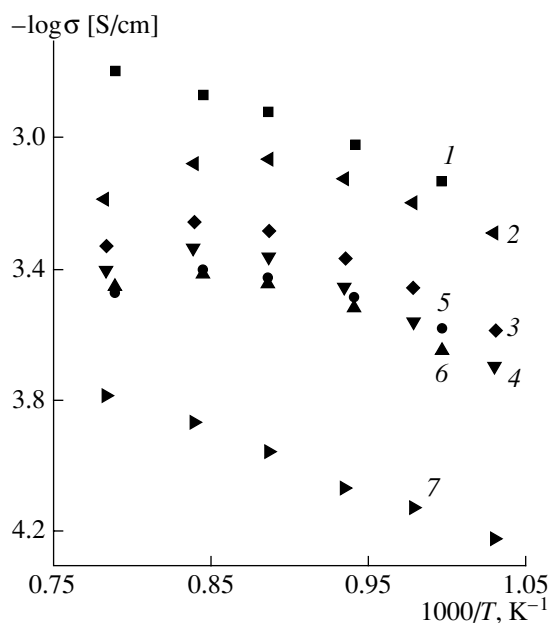


Fig. 6. Temperature dependences of protonic conductivity for (1) $0.995(0.50\text{YO}_{1.5} + 0.50\text{LaO}_{1.5}) + 0.005\text{CaO}$, (2) $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, (3) $\text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, (4) $\text{La}_{0.97}\text{Ca}_{0.03}\text{YO}_{3-\alpha}$, (5) $0.995(0.55\text{YO}_{1.5} + 0.45\text{LaO}_{1.5}) + 0.005\text{CaO}$, (6) $0.995(0.45\text{YO}_{1.5} + 0.55\text{LaO}_{1.5}) + 0.005\text{CaO}$, and (7) $0.995(0.90\text{YO}_{1.5} + 0.10\text{LaO}_{1.5}) + 0.005\text{CaO}$; reductive atmosphere, $p\text{O}_2 = 10^{-10}$ Pa.

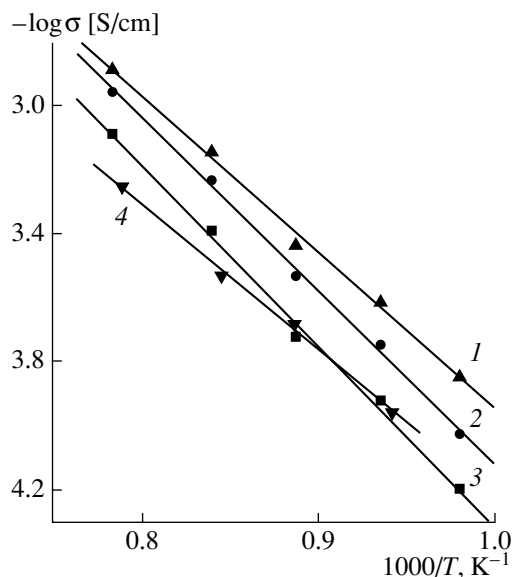


Fig. 7. Temperature dependences of oxygen conductivity for (1) $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, (2) $\text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, (3) $\text{La}_{0.97}\text{Ca}_{0.03}\text{YO}_{3-\alpha}$, and (4) $0.995(0.55\text{YO}_{1.5} + 0.45\text{LaO}_{1.5}) + 0.005\text{CaO}$; reductive atmosphere, $p\text{O}_2 = 10^{-10}$ Pa.

observed in $\text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$ with a stoichiometric Y : La ratio (1 : 1). The activation energy for oxygen conduction is 106 ± 1 kJ/mol.

CONCLUSIONS

(1) In air the materials studied are mixed ion-hole semiconductors. In the system $0.995[(1-x)\text{YO}_{1.5} + x\text{LaO}_{1.5}] + 0.005\text{CaO}$ ($x = 0.1-0.6$), the stoichiometric composition with a 1 : 1 ratio between Y and La has the maximal part and magnitude of ionic conductivity.

(2) In a reductive atmosphere, all the compositions are ionic conductors at 700–1000°C. The transport numbers reach 1.0 for ions and 0.8, for protons.

(3) The conductivity increases in the series $\text{La}_{0.97}\text{Ca}_{0.03}\text{YO}_{3-\alpha} < \text{LaY}_{0.97}\text{Ca}_{0.03}\text{O}_{3-\alpha} < \text{La}_{0.985}\text{Y}_{0.985}\text{Ca}_{0.03}\text{O}_{3-\alpha}$, i.e. the stoichiometric compound with a 1 : 1 ratio between Y and La has the highest conductivity.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-32390. Authors are grateful to Z.S. Martem'yanova for performing the x-ray diffraction analyses.

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