

Oxygen permeability of transition metal-containing La(Sr,Pr)Ga(Mg)O_{3-δ} ceramic membranes

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Acceptor-type doping of perovskite-type La_{1-x}Sr_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} (x = 0-0.20, y = 0.15-0.20, M = Fe, Co, Ni) leads to significant enhancement of ionic conductivity and oxygen permeability due to increasing oxygen vacancy concentration. The increase in strontium and magnesium content is accompanied, however, with increasing role of surface exchange kinetics as permeation-limiting factor. At temperatures below 1223 K, the oxygen permeation fluxes through La(Sr)Ga(Mg,M)O_{3-δ} membranes with thickness less than 1.5 mm are predominantly limited by the exchange rates at membrane surface. The oxygen transport in transition metal-containing La(Sr)Ga(Mg)O_{3-δ} ceramics increase in the sequence Co < Fe < Ni. The ionic conduction in these phases is, however, lower than that in the parent compounds, La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ}. The highest level of oxygen permeation, comparable to that of La(Sr)Fe(Co)O₃- and La₂NiO₄-based phases, is observed for La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} membranes. The average thermal expansion coefficients of La(Sr)Ga(Mg,M)O_{3-δ} ceramics in air are in range (11.6–18.4) × 10⁻⁶ K⁻¹ at 373–1273 K. Doping of LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} with praseodymium results in moderate increase of the permeation fluxes, lower thermal expansion and an improved phase stability in reducing environments.

Key words: ceramic membrane, mixed conductor, perovskite, lanthanum gallate, oxygen permeability

Permeabilidad de oxígeno en membranas cerámicas de La(Sr,Pr)Ga(Mg)O_{3-δ} con metales de transición.

El dopado aceptor de cerámicas tipo perovskita La_{1-x}Sr_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} (x = 0-0.20, y = 0.15-0.20, M = Fe, Co, Ni) da lugar a una mejora significativa de la conductividad iónica y de la permeabilidad al oxígeno debido al aumento de la concentración de vacantes de oxígeno. Sin embargo, el aumento de la cantidad de estroncio y magnesio viene acompañado de un aumento de la participación de las cinéticas de intercambio superficial como factor limitante de la permeabilidad. A temperaturas por debajo de 1223 K la permeabilidad al flujo de oxígeno a través de las membranas de La(Sr)Ga(Mg,M)O_{3-δ} con espesor menor de 1.5 mm está limitado principalmente por las velocidades de intercambio en la superficie de la membrana. El transporte de oxígeno en las cerámicas La(Sr)Ga(Mg)O_{3-δ} que contienen M aumenta en la secuencia Co < Fe < Ni. La conductividad iónica en estas fases es, sin embargo, menor que en la de los compuestos La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ}. El mayor nivel de permeabilidad de oxígeno, comparable a la de las fases basadas en La(Sr)Fe(Co)O₃ y La₂NiO₄, se observa para las membranas de La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ}. Los coeficientes de dilatación térmica medios de las cerámicas La(Sr)Ga(Mg,M)O_{3-δ} en aire son del orden de (11.6–18.4) × 10⁻⁶ K⁻¹ a 373–1273 K. El dopado de LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} con praseodimio da lugar a un incremento moderado de los flujos de permeabilidad, menor dilatación térmica y una mejor estabilidad de fase en entornos reductores.

Palabras clave: membrana cerámica, conductor mixto, perovskita, galato de lantano, permeabilidad de oxígeno

1. INTRODUCTION

Dense ceramic membranes with mixed oxygen-ionic and electronic conductivity are of great interest for separation of high-purity oxygen from air and conversion of light hydrocarbons to valuable products [1-3]. In particular, the application of mixed-conducting membranes for partial oxidation of natural gas to synthesis gas is expected to substantially decrease capital investments, necessary for the gas-to-liquid plants, by integrating oxygen separation and partial oxidation of methane in a single reactor [2,3]. The materials of ceramic membrane reactors should satisfy to numerous requirements, including high oxygen semi-permeability, thermodynamic and dimensional stability in a wide range of temperatures and oxygen partial pressures, compatibility with catalyst materials, and suitable thermomechanical properties. One promising group of the membrane materials relates to LaGaO₃-based mixed conductors with perovskite structure. Substitution of La with alkaline-earth cations (Ca, Sr, Ba) and Ga with bivalent cations (Mg, Ni) results in high ionic conduction with one of the highest oxygen-ionic conductivities occurring for solid solution series La(Sr)Ga(Mg)O_{3-δ} (LSGM) [4-7]. Advantages of LSGM include relatively low thermal expansion coefficient, close to that of stabilized zirconia, and sufficient

chemical stability in a wide range of oxygen partial pressure. An increase in electronic conductivity necessary for the membrane application can be achieved by introducing of transition metal cations, such as Fe, Co or Ni, into the gallium sublattice of LaGaO₃ [7-11]. Significant oxygen permeation fluxes were observed for LaGa_{1-x}Ni_xO_{3-δ} (x = 0.20-0.50) and LaGa_{0.40}Co_{0.60-y}Mg_yO_{3-δ} (y = 0.20-0.25) dense ceramic membranes [7,9]. Oxygen permeation through such membranes is limited predominantly by the oxygen ion diffusion in ceramic bulk; the ionic contribution to total conductivity was found less than 2% at 1073-1223 K. Since ionic transport in doped lanthanum gallates occurs via the oxygen-vacancy diffusion mechanism, further acceptor doping is expected to increase vacancy concentration, ionic conductivity and, consequently, oxygen permeability. Furthermore, decreasing the concentration of transition-metal cations in the Ga sublattice is expected to result in a higher stability of ceramic membranes under high oxygen chemical potential gradients. The present work continues our research of LaGaO₃-based mixed conductors as potential membrane materials [6-10] and is focused on the studies of oxygen permeability, thermal expansion and stability of La_{1-x}A_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} (A = Sr, Pr; M = Fe, Co, Ni) ceramics.

2. EXPERIMENTAL PROCEDURE

The powders of perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.80-y}\text{Mg}_y\text{M}_{0.20}\text{O}_{3-\delta}$ ($x = 0-0.20$, $y = 0.15-0.20$, $M = \text{Fe, Co, Ni}$) and $\text{La}_{0.50}\text{Pr}_{0.50}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ were synthesized by standard ceramic technique from the stoichiometric amounts of high-purity metal oxides or salts (carbonates, nitrates or oxalates). Solid state reactions were conducted in air at 1420 to 1630 K for 20-40 hours with multiple intermediate grindings. Dense ceramic samples were pressed at 250-400 MPa and sintered in air at 1670-1820 K for 3-5 hours; the sintering temperatures are listed in Table I. In the case of $\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{M}_{0.20}\text{O}_{3-\delta}$ ($M = \text{Fe, Co}$), having a worse sinterability compared to other studied materials, the sintering aid of Bi_2O_3 (5 wt%) was added before pressing. At sintering temperatures used in this work, bismuth oxide was shown to completely evaporate ([12] and reference cited); the remaining amounts of Bi_2O_3 are smaller than the low detection limit of standard analytical techniques. After sintering, the ceramic samples were annealed in air at 1270 K for 3-4 hours and then slowly cooled in order to achieve equilibrium with air at low temperatures. The density of ceramics (ρ_{exp}) determined by standard picnometric technique was in range 92-97 % of their theoretical density (ρ_{theor}) calculated from the results of X-ray diffraction (XRD) studies (Table I).

TABLE I. PROPERTIES OF $\text{La}(\text{Sr,Pr})\text{Ga}(\text{Mg,M})\text{O}_{3-\delta}$ CERAMICS

Composition	Sintering temperature, K (± 10 K)	Relative density $\rho_{\text{exp}}/\rho_{\text{theor}}$ %	Unit cell parameters			
			a, nm	b, nm	c, nm	α , °
$\text{LaGa}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	1798	96.8	0.5466	-	-	60.66
$\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	1798	96.4	0.5485	-	-	60.57
$\text{La}_{0.90}\text{Pr}_{0.10}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	1798	96.0	0.5491	0.5485	0.7757	-
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Fe}_{0.20}\text{O}_{3-\delta}$	1820	92.1	0.5506	-	-	60.18
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Co}_{0.20}\text{O}_{3-\delta}$	1673	91.7	0.5474	-	-	60.37

The characterization of ceramic materials included XRD (Rigaku Geigerflex D/MAX-B), scanning electron microscopy combined with energy dispersive analysis (Hitachi S-4100), dilatometry (Linseis L70/2001), measurements of the total conductivity as function of temperature and oxygen partial pressure (4-probe DC), faradaic efficiency studies, and determination of steady-state oxygen permeation fluxes. Detailed description of experimental equipment and procedures was published elsewhere ([6-10,13,14] and references therein). The oxygen permeation and faradaic efficiency measurements were performed in temperature range 973-1223 K. All data on the oxygen permeability presented in this paper correspond to the membrane feed-side oxygen partial pressure (p_2) equal to 21 kPa (atmospheric air). The data on faradaic efficiency were obtained in air under zero oxygen chemical potential gradient.

In this article, the oxygen permeation processes are discussed using quantities of permeation flux density j ($\text{mol}\times\text{s}^{-1}\times\text{cm}^{-2}$) and specific oxygen permeability $J(\text{O}_2)$ ($\text{mol}\times\text{s}^{-1}\times\text{cm}^{-1}$) interrelated as [7,13]:

$$j = \frac{J(\text{O}_2)}{d} \ln \left[\frac{p_2}{p_1} \right]$$

where d is the membrane thickness, and p_1 is the membrane permeate-side oxygen partial pressure. The oxygen permeation flux through a ceramic membrane may depend on the ambipolar conductivity of ceramic bulk and oxygen exchange rates at the membrane surface [1]. The quantity $J(\text{O}_2)$ is suitable to identify a limiting effect of surface exchange kinetics on the oxygen permeation by analyzing dependence of the permeation flux on membrane thickness. As $J(\text{O}_2)$ is proportional

to $j \times d$, the specific oxygen permeability should be thickness-independent when the surface exchange limitations are negligible. When the exchange rate affects the overall oxygen transfer, the values of $J(\text{O}_2)$ should increase with d at a given oxygen chemical potential due to decreasing role of the exchange kinetics.

Oxygen transference numbers (t_{O}) were determined from the results of faradaic efficiency studies. The ionic conductivity (σ_{O}) was calculated from the data on transference numbers and total conductivity. As discussed below, the oxygen transport through $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.80-y}\text{Mg}_y\text{M}_{0.20}\text{O}_{3-\delta}$ ceramics at temperatures below 1173 K and membranes thickness less than 1.5 mm is predominantly limited by oxygen exchange on the membrane surface. In the case of significant surface limitations, the apparent values of transference numbers and ionic conductivity may be lower than the true values [14]. However, due to catalytically-active electrode layers applied onto the membrane surface in the case of faradaic efficiency tests, the ion transference numbers determined by this method are essentially unaffected by the surface-exchange processes and are very close to true values [14]. In this paper, the ionic transport parameters were calculated from the results of faradaic efficiency measurements with a fixed membrane thickness, 1.00 ± 0.01 mm.

3. RESULTS AND DISCUSSION

3.1. Phase composition and crystal structure

XRD analysis confirmed the formation of perovskite phase for all prepared materials. $\text{LaGa}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ ceramics was found single-phase. Traces of additional impurity phases, such as SrLaGaO_4 or MgO , were detected for other materials. The intensity of strongest impurity peaks did not exceed 2-5 % of the most intense reflection of perovskite phase. Most probably, the presence of impurity phases is due to uncompleted solid-state reactions [15]. Minor traces of secondary phases of La-Sr-Ga-O system and/or MgO are common for LaGaO_3 -based ceramics [5,15], and it can be assumed that they do not affect noticeably the transport properties. The perovskite-type lattice of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.80-y}\text{Mg}_y\text{M}_{0.20}\text{O}_{3-\delta}$ is rhombohedrally distorted (space group $R3c$). Substitution of lanthanum with praseodymium results in lower lattice symmetry; the structure of $\text{La}_{0.50}\text{Pr}_{0.50}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ was identified as orthorhombic GdFeO_3 -type perovskite (S.G. $Pbmm$). The unit cell parameters calculated from XRD data are listed in Table I.

3.2. Surface limitations of oxygen permeation

The results on oxygen permeation through $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{0.80-y}\text{Mg}_y\text{M}_{0.20}\text{O}_{3-\delta}$ ($M = \text{Fe, Co, Ni}$) dense ceramics showed that, when membrane thickness is less than 1.5 mm and temperature is below 1223 K, the overall oxygen transport is predominantly limited by the oxygen exchange on the membrane surface. As an example, Fig.1 presents selected data on the permeation fluxes and specific oxygen permeability for $\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Co}_{0.20}\text{O}_{3-\delta}$ membranes. The permeation fluxes decrease with increasing d at 1223 K and are almost independent of the thickness at ≤ 1173 K, whilst the oxygen permeability increases. This unambiguously indicates the presence of significant surface limitations, the role of which becomes greater with decreasing temperature.

One should note that, for lanthanum gallate - based phases containing smaller amounts of the alkaline-earth cation, the only permeation-limiting factor at 1073-1223 K is the bulk ionic conductivity [7,9]. In particular, the specific oxygen permeability of $\text{LaGa}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.20-0.50$) and $\text{LaGa}_{0.40}\text{Co}_{0.60-y}\text{Mg}_y\text{O}_{3-\delta}$ ($y = 0.20-0.25$) membranes was found independent of the membrane thickness at $d > 0.50$ mm, whereas

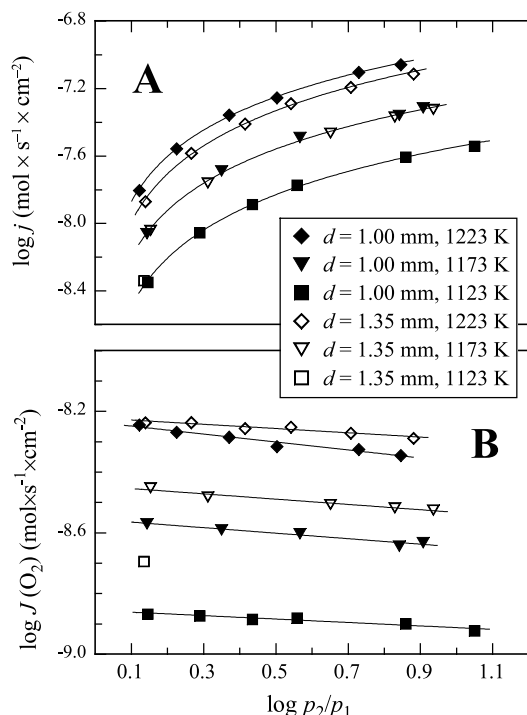


Fig.1. Dependence of oxygen permeation fluxes (A) and specific oxygen permeability (B) of La_{0.80}Sr_{0.20}Ga_{0.60}Mg_{0.20}Co_{0.20}O_{3-δ} membranes on the oxygen partial pressure gradient.

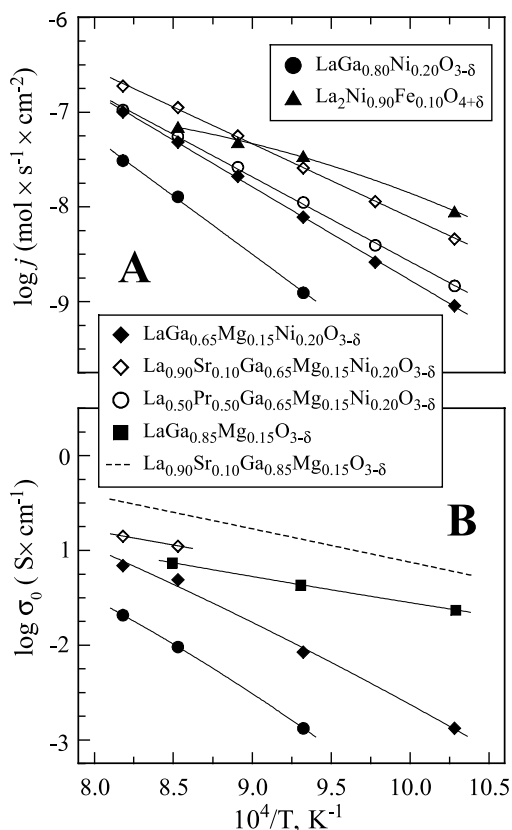


Fig.2. Temperature dependence of oxygen permeation fluxes through La(Sr,Pr)Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} membranes under fixed oxygen partial pressure gradient ($d = 1.00$ mm, $p_1 = 2.1$ kPa, $p_2 = 21$ kPa) (A), and oxygen ionic conductivity of Ni-containing LaGaO₃ ceramics as estimated from the data on faradaic efficiency and total conductivity in air (B). Data on LaGa_{0.80}Ni_{0.20}O_{3-δ} [6,7], LaGa_{0.85}Mg_{0.15}O_{3-δ} [6], La_{0.90}Sr_{0.10}Ga_{0.85}Mg_{0.15}O_{3-δ} [5] and La₂Ni_{0.90}Fe_{0.10}O_{4+δ} [13] are shown for comparison.

the permeation fluxes increased with decreasing thickness [7,9]. The results of faradaic efficiency tests on La_{1-x}Sr_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} (M = Fe, Co, Ni) membranes suggest that the ionic contribution to total conductivity of these ceramic materials is less than 25-28 % at 1223 K and decreases at lower temperatures. Hence, increasing concentration of the acceptor-type dopants in the perovskite lattice of LaGa(M)O_{3-δ} is accompanied with increasing role of surface exchange kinetics, whilst the oxygen transfer through membrane bulk is mainly determined by the ionic conductivity.

One attempt to suppress limiting effect of the surface exchange was made by substituting 50% of lanthanum cations in LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} with praseodymium. Praseodymium oxide is known to exhibit high catalytic activity in reactions involving oxygen (e.g. [12]). Indeed, this type of doping resulted in moderate increase in oxygen permeation fluxes at temperature below 1223 K (Fig.2A). However, such an improvement is rather insufficient, and further development of surface activation of La(Sr)Ga(Mg,M)O_{3-δ} membranes is necessary.

3.3. Oxygen ionic transport vs. cation composition

Figs.2A and 3A present temperature dependencies of the oxygen permeation fluxes through LaGaO₃-based membranes at fixed oxygen pressure gradient. The Arrhenius plots of ionic conductivity of La_{1-x}Sr_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} ceramics in air, estimated from results of faradaic efficiency and total conductivity measurements, are shown in

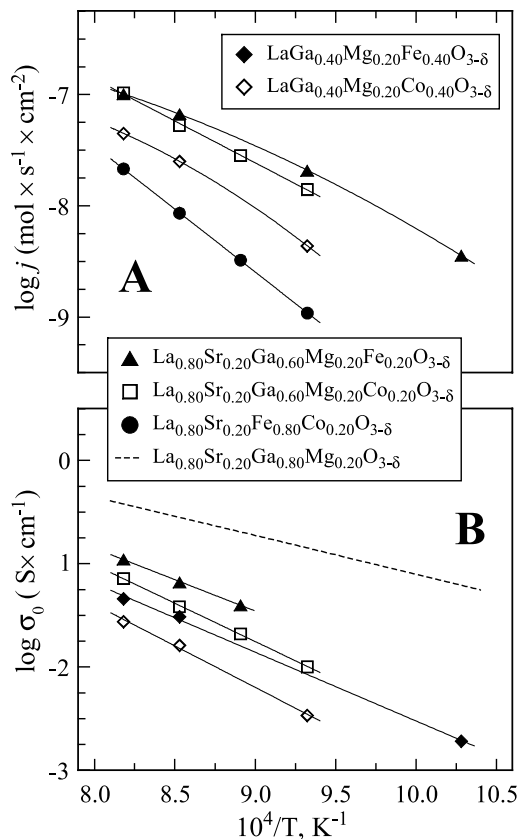


Fig.3. Temperature dependence of oxygen permeation fluxes through La_{0.80}Sr_{0.20}Ga_{0.60}Mg_{0.20}O_{3-δ} (M = Fe, Co) membranes under fixed oxygen partial pressure gradient ($d = 1.00$ mm, $p_1 = 2.1$ kPa, $p_2 = 21$ kPa) (A), and oxygen ionic conductivity of LaGaO₃-based ceramics as estimated from the data on faradaic efficiency and total conductivity in air (B). Data on La_{0.80}Sr_{0.20}Ga_{0.80}Mg_{0.20}O_{3-δ} [5], La_{0.80}Sr_{0.20}Fe_{0.80}Co_{0.20}O_{3-δ} and LaGa_{0.40}Mg_{0.20}M_{0.40}O_{3-δ} [9,10] are shown for comparison.

Figs.2B and 3B. As expected, acceptor-type doping with strontium and magnesium leads to increasing oxygen vacancy concentration and, hence, higher ionic conductivity and oxygen permeability. At the same time, it should be mentioned that the concentration of alkaline-earth cations in the studied compositions is close to their solubility limits in LaGaO_3 lattice [4,5]; further additions lead to the intensive segregation of secondary phases and deterioration of the ionic transport.

The oxygen ionic conductivity of transition metal-containing LaGaO_3 is lower with respect to parent compounds, $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (Figs.2B and 3B). The values of activation energy (E_A) for ionic transport, calculated using standard Arrhenius model, are 70-80 kJ/mol for LSGM and 120-170 kJ/mol for $\text{La}(\text{Sr})\text{Ga}(\text{Mg},\text{M})\text{O}_{3-\delta}$ (Table II). This difference can be explained by local ordering in oxygen sublattice, resulting from either associations of oxygen vacancies with bivalent cation (Mg^{2+} , Sr^{2+} , M^{2+}) or formation of stable $\text{M}^{4+}\text{-O-Mg}^{2+}$ clusters where tetravalent cations inhibit oxygen ion migration through Coulombic attraction [6]. The ordering phenomena may take place up to temperatures higher than the characteristic temperature of order-disorder transition in $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$, 870±50 K [5]. For instance, partial ordering of oxygen vacancies forming microdomains in $(\text{La},\text{Sr})\text{CoO}_{3-\delta}$ perovskites at high values of δ was detected up to temperatures as high as 1170 K [16]. For Ni-containing gallates, the activation energy tends to decrease at temperatures above 1200 K and the ionic conductivity approach that of undoped material (Fig.2B); the critical temperature of order-disorder transition would therefore appear to be close to 1300 K.

TABLE II. ACTIVATION ENERGY FOR OXYGEN IONIC CONDUCTIVITY IN LaGaO_3 -BASED PHASES

Composition	T, K	E_A , kJ/mol	Ref.
$\text{LaGa}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	973 – 1223	171 ± 8	This work
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Fe}_{0.20}\text{O}_{3-\delta}$	1123 – 1223	126 ± 3	This work
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Co}_{0.20}\text{O}_{3-\delta}$	1073 – 1223	152 ± 2	This work
$\text{LaGa}_{0.40}\text{Mg}_{0.20}\text{Fe}_{0.40}\text{O}_{3-\delta}$	973 – 1223	135 ± 19	[10]
$\text{LaGa}_{0.40}\text{Mg}_{0.20}\text{Co}_{0.40}\text{O}_{3-\delta}$	1073 – 1223	163 ± 8	[10]
$\text{LaGa}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$	873 – 1173	72 ± 5	[6]
$\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{3-\delta}$	> 873	76 ± 1	[5]
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.80}\text{Mg}_{0.20}\text{O}_{3-\delta}$	> 873	81 ± 1	[5]

Both the ionic conductivity and oxygen permeability of $\text{La}(\text{Sr})\text{Ga}(\text{Mg},\text{M})\text{O}_{3-\delta}$ increases in the sequence $\text{M} = \text{Co} < \text{Fe} < \text{Ni}$ (compare Figs.2 and 3). The lower oxygen ionic conduction in Fe- and Co-doped gallates can be attributed to stronger Fe-O and Co-O bonds compared to Ni-O, due to anomalous oxidation state of nickel with respect to iron and cobalt. In particular, oxygen-vacancy diffusion coefficients in the perovskite-type compounds increase in the sequence $\text{Cr} < \text{Fe} < \text{Co}$ [17,18], implying that the next member of the series, Ni, has still higher diffusion coefficient. The faster ionic transport in Fe-containing gallates compared to Co-substituted analogues (Fig.3) is associated, most probably, with structural features, namely the larger unit cell volume and smaller distortion of the crystal lattice (Table I and [10]) resulting in more degenerate system of the oxygen-vacancy hopping pathways.

For the studied series of compositions, the highest oxygen-ionic transport was observed for $\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ ceramics (Figs.2 and 3). The permeability of this material is more than 10 times higher compared to $\text{La}_{0.80}\text{Sr}_{0.20}\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$, one representative of $(\text{La},\text{Sr})\text{Fe}_{0.80}\text{Co}_{0.20}\text{O}_{3-\delta}$ series suggested for the membrane application, and is similar to that of La_2NiO_4 -based solid solutions, another promising group of membrane materials.

3.4. Thermal expansion

The average thermal expansion coefficients of $\text{La}(\text{Sr})\text{Ga}(\text{Mg},\text{M})\text{O}_{3-\delta}$ ceramics, calculated from the dilatometric data in air (Fig.4), are in the range $(11.6\text{-}18.4) \times 10^{-6} \text{ K}^{-1}$ (Table III). The acceptor-type doping with strontium and magnesium leads to a moderate increase in thermal expansion due to increasing oxygen vacancy concentration. The dilatometric curves show a nonlinear behavior at temperatures above 770-960 K, most likely due to oxygen losses from the perovskite lattice on heating. This phenomenon, typical for thermal expansion of perovskite-type phases containing transition metal cations, results from chemically-induced expansion associated with increasing oxygen nonstoichiometry and, as a consequence, changes in oxidation states and radii of variable-valence ions [19,20]. The addition of praseodymium results in an opposite effect: the thermal expansion of $\text{La}_{0.50}\text{Pr}_{0.50}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ is lower than that of parent phase, $\text{LaGa}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$ within all studied temperature range (Fig.4). Since praseodymium cations in air exist in two oxidation states, 3+ and 4+ (e.g. [21]), this phenomenon can be attributed to decreasing oxygen nonstoichiometry when La^{3+} is substituted with Pr^{4+} .

TABLE III. AVERAGE THERMAL EXPANSION COEFFICIENTS OF $\text{La}(\text{Sr},\text{Pr})\text{Ga}(\text{Mg},\text{M})\text{O}_{3-\delta}$ CERAMICS IN AIR

Composition	T, K	$(\bar{\alpha} \times 10^6) \pm 0.1, \text{ K}^{-1}$
$\text{LaGa}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	373 – 773	11.6
	773 – 1273	17.0
$\text{La}_{0.90}\text{Sr}_{0.10}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	373 – 773	12.0
	773 – 1273	18.4
$\text{La}_{0.50}\text{Pr}_{0.50}\text{Ga}_{0.65}\text{Mg}_{0.15}\text{Ni}_{0.20}\text{O}_{3-\delta}$	373 – 923	9.2
	923 – 1273	14.5
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Fe}_{0.20}\text{O}_{3-\delta}$	373 – 923	10.8
	923 – 1100	17.5
$\text{La}_{0.80}\text{Sr}_{0.20}\text{Ga}_{0.60}\text{Mg}_{0.20}\text{Co}_{0.20}\text{O}_{3-\delta}$	373 – 960	13.4
	960 – 1100	17.5

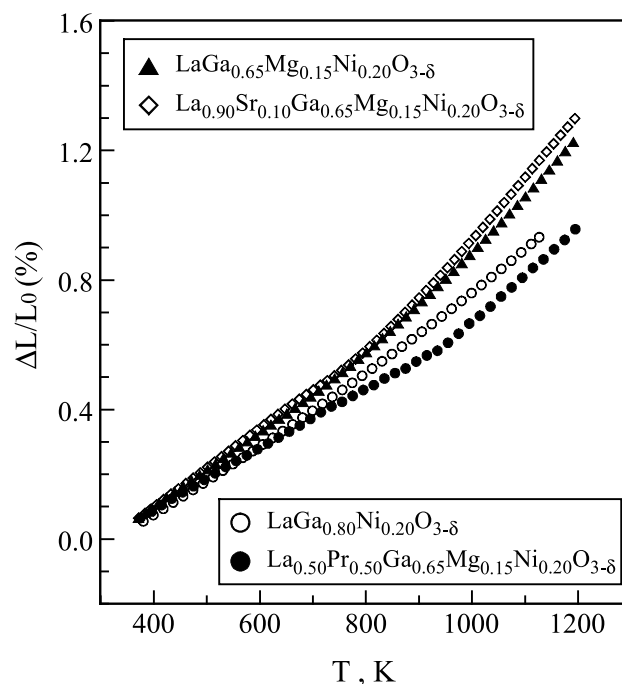


Fig.4. Dilatometric curves of Ni-containing LaGaO_3 -based ceramics in air. Data on $\text{LaGa}_{0.80}\text{Ni}_{0.20}\text{O}_{3-\delta}$ [7] are shown for comparison.

3.5. Phase stability of Ni-containing gallates

The phase stability boundaries of La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} and La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} ceramics under reduced oxygen partial pressure were evaluated from the results on p(O₂)-dependencies of the total conductivity. One example of stability limit determination is illustrated by inset in Fig.5 for La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} at 1023 K. The oxygen pressure, at which the slope of log(σ) – log p(O₂) curves started to change, was considered as the stability boundary at a given temperature. Further reducing of oxygen partial pressure lead to drastic degradation of conductivity due to phase decomposition. In literature (e.g. Ref.[22,23]), the stability limits of oxide materials evaluated from the data on p(O₂)-dependencies of total conductivity are in excellent agreement with the results obtained by other methods, such as isothermal gravimetric analysis in atmospheres with controlled p(O₂).

The decomposition of La(Sr,Pr)Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} perovskites occurs at oxygen pressures substantially lower than that of NiO (Fig.5), thus suggesting stabilization of nickel oxidation state by the structural environment in perovskite lattice. The low-p(O₂) stability limit of La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} is quite similar to that of La₂NiO_{4+δ} reported in literature. At the same time, La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} decomposes at oxygen pressures 10²-10⁴ times lower than Sr-containing gallate, being stable down to p(O₂) values as low as 10⁻¹⁷-10⁻¹⁰ Pa at 1023-1223 K (Fig.5). Most likely, such an enhancement results from increasing oxygen content due to incorporation of praseodymium cation, having the average oxidation state higher than 3+ and thus stabilizing the lattice. In the case of La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} in reducing atmospheres nickel cations are expected to be mostly divalent, forming oxygen-deficient Ni-O octahedra in the lattice; this state is similar to La₂NiO₄ phase, leading to similar phase existence domain.

In summary, due to significant surface limitations to oxygen transport, all studied materials exhibit comparable level of oxygen permeability. The only exception is La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} membranes showing 2-3 times higher oxygen permeation. At the same time, stability of the latter phase is insufficient for the operation under large oxygen chemical potentials, such as air/methane, at temperatures above 1000-1050 K. In addition, La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} ceramics have a relatively high thermal expansion coefficient, 18.4×10⁻⁶ at 773-1273 K, limiting the compatibility with other materials of electrochemical membrane reactors. The data on phase stability and oxygen permeation suggest that a better performance for the membrane applications may be achieved by combining of acceptor-type doping of La(Ga,M)O_{3-δ} with incorporation of higher-valence cations having high catalytic activity, such as praseodymium or cerium. In particular, La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} ceramics possess a significant permeability, moderate TECs and an improved stability in reducing environments.

4. CONCLUSIONS

Dense membranes of perovskite-type La_{1-x}Sr_xGa_{0.80-y}Mg_yM_{0.20}O_{3-δ} (x = 0-0.20, y = 0.15-0.20, M = Fe, Co, Ni) and La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} were prepared by the standard ceramic synthesis route. The average thermal expansion coefficients of La(Sr)Ga(Mg,M)O_{3-δ} ceramics in air are in range (11.6-18.4)×10⁻⁶ K⁻¹ at 373-1273 K. Doping of LaGa(M)O_{3-δ} with strontium and magnesium results in a considerable enhancement of the ionic conductivity and oxygen permeability due to increasing oxygen vacancy concentration. This is accompanied, however, with increasing role of surface exchange as a permeation-limiting factor. At temperatures below 1223 K, the oxygen permeation fluxes through dense La(Sr)Ga(Mg,M)O_{3-δ} membranes with thickness less than 1.5

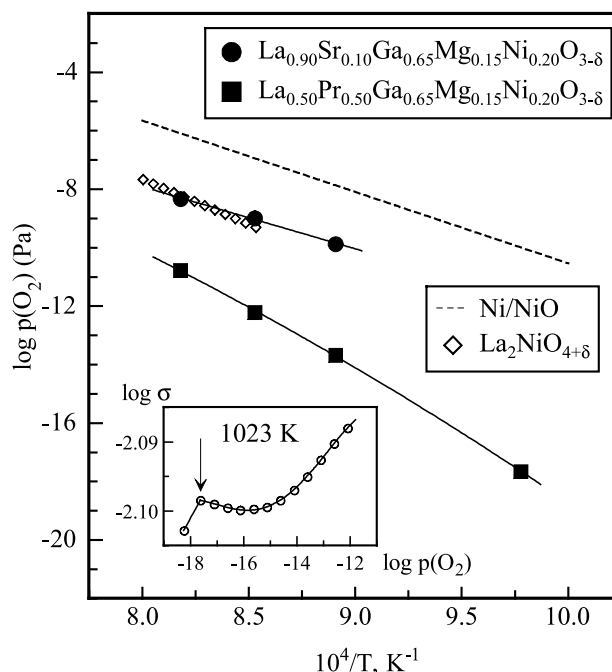


Fig.5. Phase stability boundaries of LaGaO₃-based materials under reducing conditions. Literature data on NiO [24] and La₂NiO_{4+δ} [25] are shown for comparison. Inset illustrates determination of the stability limit for La_{0.50}Pr_{0.50}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} at 1023 K.

mm are mainly limited by the exchange kinetics on the membrane surface. The ionic transport in transition metal-containing gallates, characterized by activation energies varying in the range 126-171 kJ/mol, is lower with respect to parent compounds, La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} where E_A values are 70-80 kJ/mol. This behavior indicates an increased role of defect association when gallium is substituted with transition metal cations. Both the ionic conductivity and oxygen permeability of La(Sr)Ga(Mg,M)O_{3-δ} ceramics increases in the sequence Co < Fe < Ni. The highest level of oxygen permeability, comparable to that of La(Sr)Fe(Co)O_{3-δ} and La₂NiO_{4+δ}-based solid solutions, is observed for La_{0.90}Sr_{0.10}Ga_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} membranes. Partial substitution of lanthanum with praseodymium results in moderate increase in the permeation fluxes, lower thermal expansion and considerable enhancement of stability at reduced oxygen partial pressures.

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