

Thermal and chemical induced expansion of $\text{La}_{0.3}\text{Sr}_{0.7}(\text{Fe},\text{Ga})\text{O}_{3-\delta}$ ceramics

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Abstract

The linear thermal expansion coefficients (TECs) of perovskite-type $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0-0.4$), determined by dilatometric and high-temperature X-ray diffraction techniques, are in the range $(19-41)\times 10^{-6} \text{ K}^{-1}$ at 770–1170 K, decreasing when the oxygen partial pressure or gallium concentration increases. At oxygen pressures from 10^{-4} to 1 atm, the isothermal chemically induced expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics is a linear function of the oxygen nonstoichiometry. The magnitude of changes in δ and, thus, chemical expansion both are reduced by gallium doping. The ratio between isothermal chemical strain and nonstoichiometry variations, $(\epsilon_C/\Delta\delta)$, follows an Arrhenius-type dependence on temperature and varies in the range $(1.7-5.9)\times 10^{-2}$. The drastic increase in the thermal expansion at temperatures above 700 K, typical for ferrite-based ceramics, was shown to be mainly apparent, resulting from the chemically-induced expansion of the lattice due to oxygen losses. The TEC values, corrected for the chemical strain on heating, are close to the TECs at low temperatures and increase with gallium content. The observed correlations between the thermal and chemical expansion and ionic conductivity of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ are discussed in terms of their relationships with the oxygen deficiency and cation composition.

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1. Introduction

Dense ceramic membranes with mixed oxygen-ionic and electronic conductivity are of great interest for applications in electrocatalytic reactors for oxygen separation and conversion of light hydrocarbons to value-added products, particularly the conversion of natural to synthesis gas.¹⁻⁵ Conventional technologies for natural gas conversion are based on steam reforming and/or partial oxidation processes. Whilst steam reforming of methane is energy-intensive due to highly endothermic nature of reaction, the most significant cost associated with partial oxidation is that of an oxygen plant. Technologies based on ion-conducting membranes may have considerable economic benefits due to

the possibility to combine oxygen separation from air and partial oxidation in a single reactor.^{4,5}

The ceramic membrane materials should satisfy to numerous requirements, including high oxygen semi-permeability, chemical and structural integrity within a wide range of temperature and oxygen partial pressure, and suitable thermomechanical properties. However, mixed-conducting ceramics known at present exhibit various specific disadvantages, which limit their applicability for the membrane reactors. In particular, strontium ferrite-based perovskite-like solid solutions exhibit attractively high oxygen permeation fluxes, but are thermodynamically and/or dimensionally unstable under large oxygen chemical potential gradients.⁶⁻¹³ Losses of lattice oxygen under reducing environments and subsequent changes in the oxidation state of iron cations result in unfavorable expansion of the lattice and differential strain across the membrane. This, in turn, induces mechanical stresses that may cause fracture of

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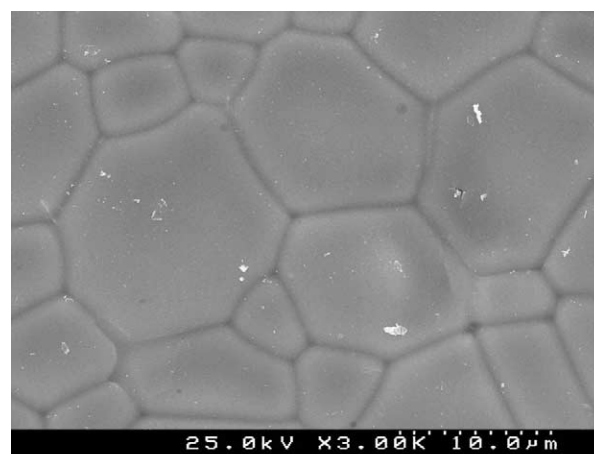
the membrane ceramics. To some extent, the stability of $\text{SrFeO}_{3-\delta}$ -based materials can be improved by partial substitution of iron with metal cations having a more stable oxidation state under the reactor operation conditions, such as Cr,^{11–13} Ti^{13,14} or Ga.^{9,10} For example, $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$ membranes were successfully tested for 500 h at 1373 K in synthesis gas generation simulating experiments.¹¹ However, doping with either chromium or titanium leads to a decrease in the ionic conductivity and, hence, a lower oxygen permeability of strontium ferrite-based materials.^{14,15}

One alternative approach to enhance the membrane stability refers to incorporation of stable trivalent cations, such as Ga or Al, into the iron sublattice of the perovskite-like ferrites. As shown in previous work,^{16–19} perovskite-related $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ phases exhibit a noticeable level of oxygen-ion conductivity at 923–1223 K in a wide range of oxygen partial pressure varying from 10^{-19} to 0.21 atm. In oxidizing conditions [$p(\text{O}_2) > 10^{-5}$ atm] these compounds possess a cubic perovskite-type structure, whereas decreasing oxygen chemical potential leads to various types of oxygen-vacancy ordering.^{16,19} The oxygen ionic conductivity of $\text{La}_{0.3}\text{Sr}_{0.7}(\text{Fe,Ga})\text{O}_{3-\delta}$ was found essentially independent of the oxygen nonstoichiometry and vacancy ordering.¹⁷ The present work continues our study of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics as potential membrane materials and is focused on the study of thermal and isothermal chemically-induced expansion. Particular emphasis is given to analysis of the effect of Ga doping, which suppresses lattice strain on oxygen chemical potential variations.^{10,17} Data on thermal expansion in air, presented in this work, are refined with respect to preliminary experiments¹⁷

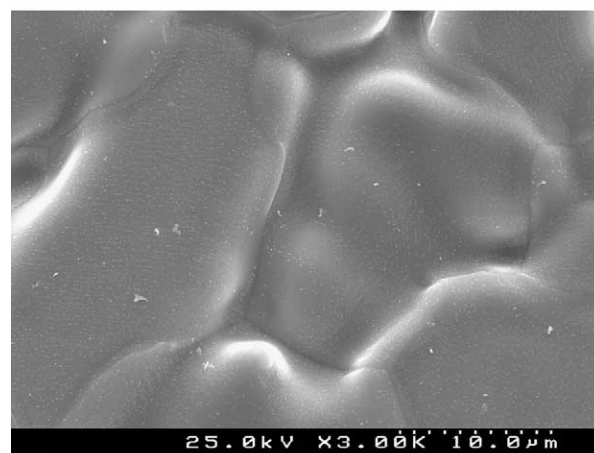
2. Experimental

Dense ceramic samples of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0-0.4$) were prepared by a standard solid state synthesis route as described elsewhere.¹⁷ Before weighting of the stoichiometric amounts of high-purity SrCO_3 , La_2O_3 , $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and Ga_2O_3 , binary oxides of lanthanum and gallium were annealed in air at 1270 K for 3–4 h. The starting mixtures were dissolved in a solution of nitric acid, dried and then calcined at moderate temperature to form fine, homogeneous powders. The solid state reactions were conducted in air at 1470 to 1640 K for 20–40 h with multiple intermediate grinding steps. Dense ceramic samples were pressed at 250–400 MPa and then sintered in air for 3–5 h. Sintering of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics with $x=0, 0.2$ and 0.4 was performed at 1560, 1650 and 1690 K (± 10 K), respectively; the sintering temperatures were selected empirically, from the results on the density and gas-tightness vs. sintering conditions. After sintering, the

samples were annealed in air at 1170 K for 4–5 h and slowly furnace-cooled in order to obtain oxygen content as close as possible to equilibrium at room temperature. The density of the ceramic materials determined by the standard picnometric technique was in the range 92.5–93.5% of their theoretical density, calculated from the results of X-ray diffraction (XRD) studies. The cation composition of selected ceramic samples was verified by ion-coupled plasma (ICP) spectroscopic analysis; scanning electron microscopy combined with energy dispersive spectroscopy (SEM-EDS) suggested uniform distribution of cations along grains and grain boundaries. Examples of SEM micrographs, reflecting microstructures typical for the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics, are presented in Fig. 1. The average grain size was found to increase with gallium additions from 7–10 μm ($x=0$) to 18–30 μm ($x=0.4$). SEM also indicated liquid phase formation at the grain boundaries of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics at $x \geq 0.2$. Most probably, both features are due to the increase in the



(a)



(b)

Fig. 1. SEM micrographs of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics with $x=0$ (a) and 0.4 (b).

Table 1
Linear thermal expansion coefficients (TECs) of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ in air, calculated from high-temperature XRD and dilatometric data

x	$\bar{\alpha} \times 10^6, \text{K}^{-1}$	
	XRD (773–1173 K)	Dilatometry (773–1148 K)
0	25.18	24.89
0.2	23.64	23.76
0.4	21.79	21.47

sintering temperature necessary to obtain gas-tight ceramics of Ga-doped lanthanum-strontium ferrites.

The results of structural characterization of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$, performed using XRD and neutron diffraction data, were reported elsewhere.^{18,19} Detailed data on the physicochemical and transport properties of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$, including partial ionic and electronic conductivities, transference numbers and oxygen permeability, were also published earlier.^{16–19}

Thermal expansion measurements in air were carried out on heating from room temperature to 1170 K using a quartz dilatometer DKV-5A and an alumina Linseis dilatometer, with a constant heating rate of 3 K/min. For these two dilatometers, the size of rectangular ceramic samples was $2 \times 2 \times 30 \text{ mm}^3$ and $6 \times 5 \times 5 \text{ mm}^3$, respectively. The reproducibility error of the thermal expansion coefficient (TEC) values was lower than 5–7%. The measurements of the thermal expansion in Ar–O₂ mixtures with various $p(\text{O}_2)$ and the isothermal chemically-induced expansion were performed at 700–1160 K, using a quartz dilatometer equipped with mechanical sensor 6MH4S and bar-shaped samples ($2 \times 2 \times 30 \text{ mm}^3$). The experiments were carried out in flowing Ar–O₂ mixtures (flow rate of 4 l/h), where the oxygen partial pressure varied from 1×10^{-4} to 1.0 atm by supplying appropriate gases and electrochemical oxygen pumping using a solid-electrolyte cell made of yttria-stabilized zirconia (YSZ) with Pt electrodes. The $p(\text{O}_2)$ values in gas mixtures supplied to the dilatometer were measured by an electrochemical YSZ sensor. In addition to the standard calibration procedures, thermal expansion

data at $p(\text{O}_2) = 0.21 \text{ atm}$ (atmospheric air) were verified by comparison with results from two other devices.

The values of TECs obtained in this work were also validated by the high-temperature XRD method. The XRD patterns were collected in air at 773–1173 K using a Philips X'Pert diffractometer (CuK_α radiation, step 0.02° , 3 s/step). The heating/cooling rate was 3 K/min; at each temperature the samples were equilibrated for 30–120 min before data acquisition. The results of structure refinement of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ are found elsewhere.^{18,19} Table 1 compares the values of linear thermal expansion coefficients ($\bar{\alpha}$), calculated from dilatometric and high-temperature XRD data. Within the limits of experimental uncertainty, the TEC values obtained by the different techniques are similar, which validates these results and indicates that the heating rate in the dilatometric experiments was small enough to provide equilibration. Similar conclusion was drawn from the good reproducibility of TECs for samples with different prehistory; an example is given in Table 2. The TEC values, measured at temperatures above 700 K when the oxygen exchange between the ceramics and gas phase is fast enough, were essentially independent of the thermal prehistory, within the limits of standard experimental error.

The oxygen nonstoichiometry values used in this work for the analysis of chemical expansion as a function of the oxygen partial pressure, were obtained by coulometric titration.¹⁹ Detailed results on the oxygen deficiency of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ (so-called $p(\text{O}_2)$ – T – δ diagrams), an example of which is shown in Fig. 2, can also be found in Ref. 19. In the course of the strain analysis, data points on chemical expansion are compared to nonstoichiometry data points measured in the same external conditions, namely temperature and oxygen partial pressure. When the nonstoichiometry values at given T or $p(\text{O}_2)$ were unavailable, approximation of the experimental data on the oxygen deficiency was used. A linear model was used for this purpose to describe the $\log p(\text{O}_2)$ vs. $1/T$ experimental dependencies, in agreement with basic thermodynamic relations in oxides.²⁰ The approximation to $(3-\delta)$ vs. $\log p(\text{O}_2)$ dependencies was empirically selected as orthogonal 3rd degree polynomial. The quality of the approximation is

Table 2
Comparative examples of average TECs for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics with different prehistory, calculated from the dilatometric results

x	Oxygen pressure in measurement atmosphere	Prehistory	$\bar{\alpha} \times 10^6, \text{K}^{-1}$ (773–1148 K)
0	$1 \times 10^{-4} \text{ atm}$	Cycle in O ₂ (298 → 1150 → 298 K)	41.07
	$1 \times 10^{-4} \text{ atm}$	Cycle in air (298 → 1150 → 298 K)	41.05
0.4	0.21 atm	As prepared	21.47
	0.21 atm	Cycle in Ar–O ₂ mixture with $p(\text{O}_2) = 10^{-4} \text{ atm}$ (298 → 1150 → 298 K)	21.55

illustrated in Fig. 2 by solid lines connecting experimental data points.

3. Results and discussion

Fig. 3 presents one example of typical dilatometric data in air. As for other atmospheres with a fixed oxygen partial pressure, the dilatometric curves of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics consist of two parts, which may be approximated by straight lines. This behavior is typical for numerous Fe- and Co-containing

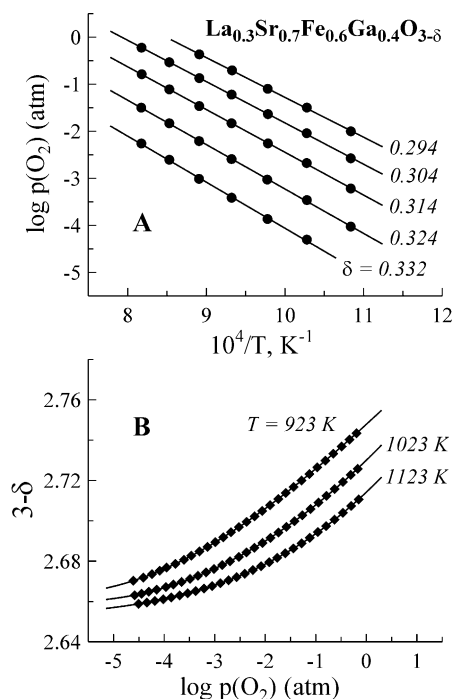


Fig. 2. Oxygen nonstoichiometry of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ perovskite as a function of temperature and oxygen partial pressure. The solid lines were obtained by approximation using linear (A) and polynomial (B) models.

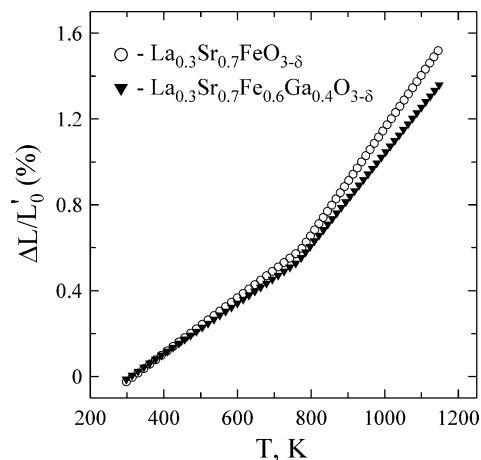


Fig. 3. Dilatometric curves of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics in air.

perovskites.^{14,21–23} As shown later, the drastic increase in the thermal expansion at temperatures above 600–750 K is mainly due to increasing oxygen nonstoichiometry on heating. The average thermal expansion coefficients, calculated from the dilatometric results in different atmospheres, are listed in Table 3. Taking into account oxygen losses from the lattice, these coefficients should be understood as apparent, resulting from a combined effect of the true thermal expansion and chemical strain of the lattice. Another necessary comment is that in the low temperature range the oxygen content and, therefore, apparent TEC values may be affected by a slow oxygen exchange with the gas phase, stagnated due to kinetic reasons. For this reason, main emphasis was given to studies of thermal and chemical expansion at temperatures above 770 K, where equilibrium with the surrounding atmosphere is more likely.

Dilatometric curves of $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$ and $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ samples in atmospheres with different $p(\text{O}_2)$ are shown in Figs. 4A and 5A; the corresponding values of the oxygen nonstoichiometry calculated from coulometric titration data¹⁹ are presented in Figs. 4B and 5B, respectively. Within the studied range of oxygen partial pressure, the apparent thermal expansion of undoped lanthanum-strontium ferrite is higher than that of the Ga-containing composition. However, the oxygen nonstoichiometry variations with temperature or oxygen pressure are also considerably larger in the case of $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$ ceramics. For example, when the temperature increases from 923 to 1123 K, the changes in δ values of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ in air are approximately 0.078 and 0.033 for $x=0$ and 0.4, correspondingly. When $p(\text{O}_2)$ increases from 1×10^{-4} to 0.21 atm at 1123 K, the oxygen content variations in these two materials are 0.127 and 0.039, respectively. This suggests that the great difference in TEC values for the undoped and Ga-containing ferrite ceramics, especially at low oxygen pressures (Table 3), is partly due to larger variation in oxygen deficiency and, hence, greater contribution of the chemical expansion to the apparent thermal expansion of

Table 3

Average TECs of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics in atmospheres with different oxygen partial pressures as calculated from the dilatometric data

x	$p(\text{O}_2)$, atm	T, K	$\bar{\alpha} \times 10^6$, K^{-1}
0	0.21	298–773	12.98
	1.0	773–1148	20.92
	0.21	773–1148	24.89
	1×10^{-4}	773–1148	41.07
0.4	0.21	298–773	11.65
	1.0	773–1148	19.08
	0.21	773–1148	21.47
	1×10^{-4}	748–1148	26.14

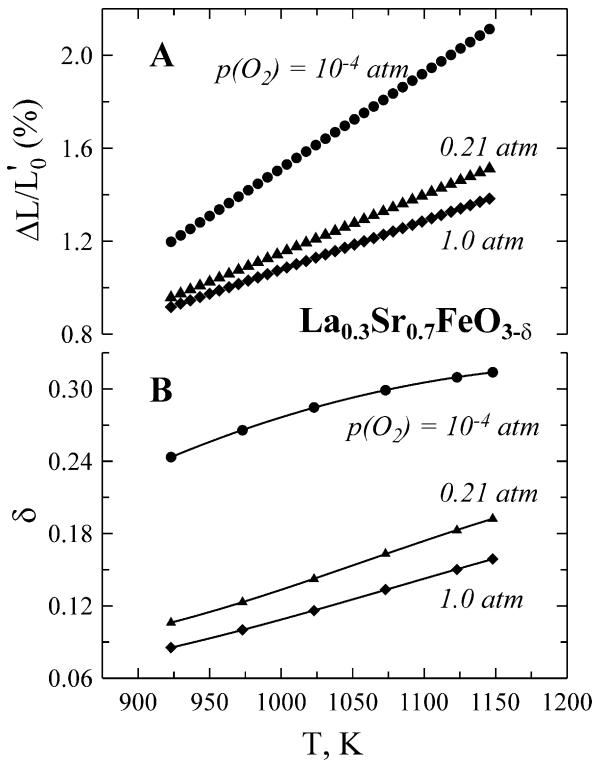


Fig. 4. Temperature dependencies of the relative elongation (A) and oxygen nonstoichiometry (B) of $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$ at various oxygen partial pressures. Solid lines are for visual guidance.

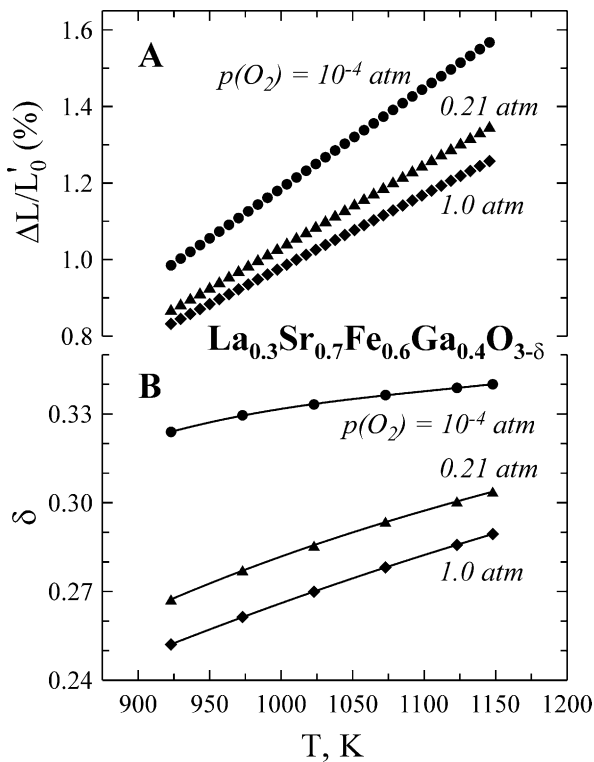


Fig. 5. Temperature dependencies of the relative elongation (A) and oxygen nonstoichiometry (B) of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ at various oxygen partial pressures. Solid lines are for visual guidance.

$\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$. At the same time, the equilibrium nonstoichiometry of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ is significantly higher than that of undoped ferrite (Figs. 4 and 5). Taking into account the correlations between oxygen-vacancy concentration and true thermal expansion, which are well known in the literature for materials with temperature-independent oxygen deficiency (e.g. Refs. 24,25), one can expect that at fixed oxygen content the lattice expansion of Ga-containing derivatives might be higher or, at least, comparable to that of $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$.

The data on isothermal chemically induced expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics as a function of oxygen pressure are given in Fig. 6. For comparison, the scale in the chemical expansion plots is chosen the same for materials with $x=0$ and 0.4. As expected from the nonstoichiometry variations, the chemically induced strain of undoped ferrite is 1.5–2.5 times greater than that of Ga-doped composition. When discussing these data, one should also mention that, due to partial oxygen-vacancy ordering and complex defect relationships in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$, the lattice parameter variations in these materials cannot be described as a simple function of the B-site cation radii.¹⁹ Therefore, the simplified model for the chemical expansion as a quantity determined mainly by the cation size changes^{26,27} cannot be applied in this case, in agreement with the conclusion

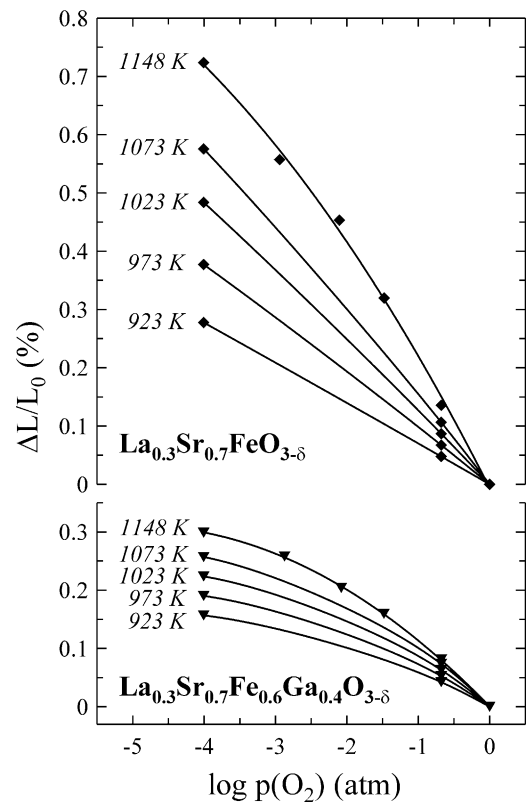


Fig. 6. Chemically-induced expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics as determined by the dilatometric measurements. Solid lines are for visual guidance only.

drawn from the analysis of literature data on $\text{LaCrO}_{3-\delta}$ -based materials.²⁸

Fig. 7 compares chemically-induced strain of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics with data on another group of mixed-conducting membrane materials, $\text{Sr}(\text{Fe},\text{Co})\text{O}_{3-\delta}$.²⁹ Perovskite-type $\text{SrFe}_{0.2}\text{Co}_{0.8}\text{O}_{3-\delta}$, which exhibits one of the highest levels of oxygen ionic conductivity among known mixed conductors,^{1,30,31} shows the maximum chemical strain; the expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ is approximately 2.5 times lower. As a first approximation, this behavior may be attributed to a higher oxygen deficiency and greater δ variations with changing $p(\text{O}_2)$ due to the high concentration of cobalt in $\text{SrFe}_{0.2}\text{Co}_{0.8}\text{O}_{3-\delta}$ phase. A lower stability and a higher nonstoichiometry are typical for Co-containing perovskites in comparison with the oxide compounds where most B sites are occupied with iron.^{21,31} The relations of the chemically-induced expansion in $\text{La}_{0.3}\text{Sr}_{0.7}(\text{Fe},\text{Ga})\text{O}_{3-\delta}$ and other types of mixed conductors, based on $\text{CeO}_{2-\delta}$ and $\text{LaCrO}_{3-\delta}$, are briefly discussed below.

The common approach, used in the literature^{28,32} to describe chemical expansion of a crystal lattice, is based on the assumption that the strain (ε_C) is a linear function of the oxygen nonstoichiometry variations. This means that, if the lattice expansion mechanism is the same within a given oxygen pressure range, the ratio ($\varepsilon_C/\Delta\delta$) should be constant. Here, the chemical strain is defined as²⁸

$$\varepsilon_C = \Delta L/L_0 \quad (1)$$

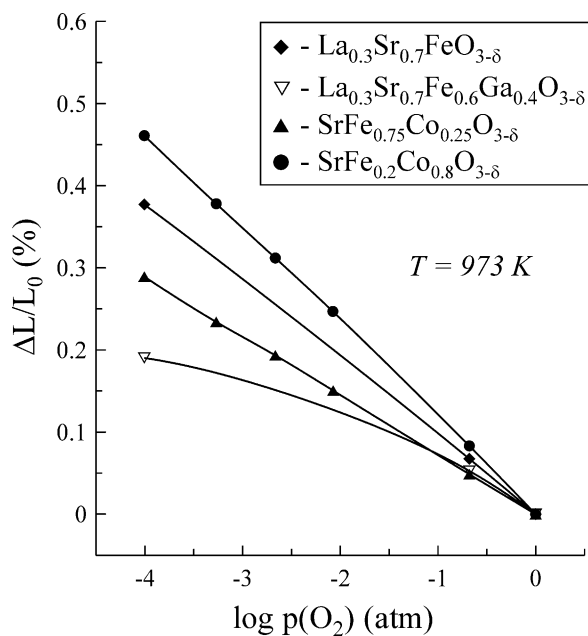


Fig. 7. Comparison of the chemically-induced strain of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ and $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics. Data on $\text{Sr}(\text{Fe},\text{Co})\text{O}_{3-\delta}$ are taken from Ref. 29.

and a suitable reference state (L_0) can be chosen, in particular, at unit oxygen pressure and the same temperature. Although this approach can be considered as a first approximation only,³² this simplification enables to quantitatively compare chemically induced expansion in materials with different nonstoichiometry and defect chemistry.²⁸ Note that in some cases, the length at room temperature is taken as the reference state.²⁶ In this work the state at room temperature is denoted as L_0' (e.g. Figs. 3–5); the reference length at the temperature of a given isothermal expansion test and unit oxygen pressure is labeled as L_0 (Figs. 6 and 7).

Fig. 8 shows data on chemical strain of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics as a function of the oxygen deficiency. For visual guidance, these results are related to the room-temperature length, L_0' . As no phase transitions occur in the studied range of the oxygen partial pressure and the structure remains cubic perovskite-type,^{16,19} the nonstoichiometry dependencies of the chemically-induced expansion can be described by a linear model, in agreement with.²⁸ Though the range of relative length variations is larger for the composition with $x=0$, the slope of $\Delta L/L_0'$ vs. δ dependencies is higher for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ ceramics (Fig. 8). This slope is proportional to the parameter ($\varepsilon_C/\Delta\delta$), which is used as a measure of the chemical strain²⁸ and plotted in Fig. 9 vs. reciprocal temperature. For materials with $x=0$ and 0.4, the temperature dependen-

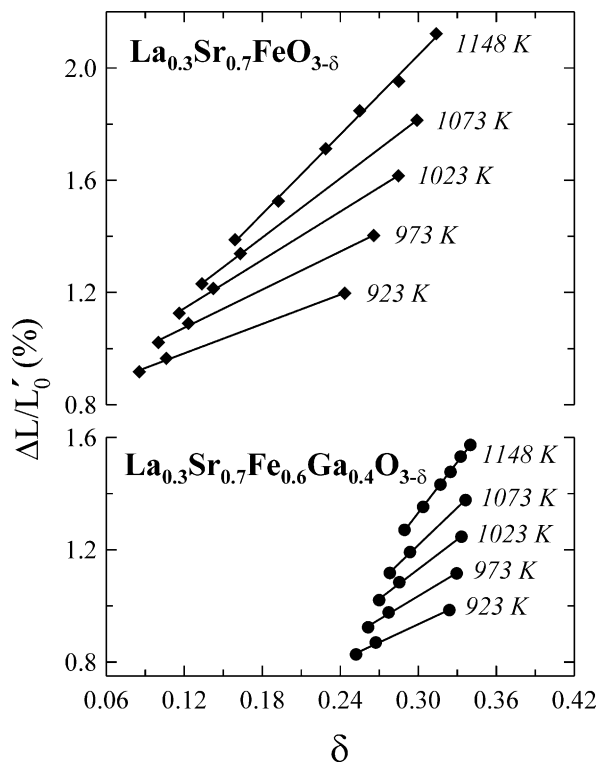


Fig. 8. Relative chemical expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ as a function of the oxygen nonstoichiometry. The strain is calculated with respect to the reference length at room temperature.

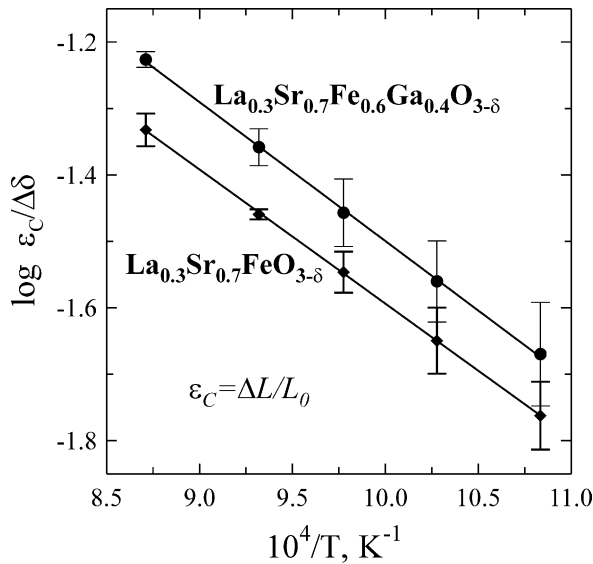


Fig. 9. Temperature dependence of the $(\epsilon_C/\Delta\delta)$ coefficient of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics.

cies of $(\epsilon_C/\Delta\delta)$ are quite similar due to the similar crystal structure and composition. The absolute values of $(\epsilon_C/\Delta\delta)$ parameter are, however, higher for Ga-containing material. Exact reasons for such behavior are still unknown. One possible explanation may refer to increasing level of structural disorder in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ when iron is substituted with gallium.¹⁹ Data on Seebeck coefficient and partial thermodynamic functions of oxygen in the lattice of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ showed that Ga doping leads to local inhomogeneities in the lattice, such as local distortions or defect clusters near gallium cations.¹⁹ Due to cation disorder in the B sublattice, this phenomenon suppresses long-range ordering and formation of vacancy-ordered microdomains, which is consistent with data on ionic conduction in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ in oxidizing atmospheres.¹⁷ Greater level of structural disorder may also explain the larger lattice chemical expansion of the Ga-containing material, related to the oxygen vacancy concentration.

Another hypothesis, which may qualitatively explain the behavior illustrated by Fig. 8, refers to a decrease in the binding energy of oxides when the oxygen nonstoichiometry increases.²⁴ Such an assumption was introduced to explain the experimentally-observed correlation between the oxygen vacancy concentration and thermal expansion of $\text{La}(\text{Sr})\text{Ga}(\text{Mg})\text{O}_{3-\delta}$ perovskites and confirmed by molecular dynamics simulations.²⁴ In general, the δ - $\bar{\alpha}$ correlations are known in the literature^{21,25,33,34} and may be explained by various factors (for example, an increase in the atomic vibration unharmonicity when the vacancy concentration increases). Nevertheless, all these factors are related to the lattice expansion via different energetic parameters;³³ the binding energy is one representative example. As the

thermal and chemically-induced expansion have similar nature, both being determined by the lattice chemical bonding, the higher values of $(\epsilon_C/\Delta\delta)$ coefficient for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ with respect to $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$ (Fig. 8) may thus be considered to result from a lower binding energy due to the higher oxygen nonstoichiometry of the former composition (Figs. 4 and 5). The decrease in the binding energy is reflected by decreasing absolute values of the partial molar enthalpy of oxygen when gallium concentration in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ increases.¹⁹

Comparison of the $(\epsilon_C/\Delta\delta)$ parameter of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ with literature data^{27,28,34} shows that lanthanum-strontium ferrite-based ceramics exhibit significantly higher chemical expansion with respect to LaCrO_3 -based materials. In particular, for B-site doped $\text{La}_{1-x}\text{A}_x\text{CrO}_{3-\delta}$ ($A = \text{Ca}, \text{Sr}$), the ratio $(\epsilon_C/\Delta\delta)$ at 1273 K varies in the range $(1.2\text{--}3.6)\times 10^{-2}$. In the case of gadolinium-doped ceria, $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$, the relative chemical strain has values comparable with that of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ at temperatures above 1120 K, but is up to 7–8 times higher than that of the ferrite-based ceramics at lower temperatures.²⁸ The $(\epsilon_C/\Delta\delta)$ parameter in doped ceria increases with increasing Gd concentration.²⁸ These trends are likely to agree with the above hypothesis on the correlation between $(\epsilon_C/\Delta\delta)$ and δ values.

The fact that the chemical strain of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics at a fixed temperature is a linear function of the oxygen nonstoichiometry (Fig. 8), enables an estimation of the true thermal expansion coefficients ($\bar{\alpha}_T$) from the apparent TECs affected by the chemically-induced expansion on heating. On heating a sample with a fixed oxygen nonstoichiometry ($\delta = \delta_1$), the expansion can be described by the coefficient

$$\bar{\alpha}_T = \frac{L_0 - L'_0}{L'_0(T_2 - T_1)} \quad (2)$$

where the physical meaning of the quantities used is illustrated by Fig. 10. For the apparent TEC

$$\bar{\alpha} = \frac{L - L'_0}{L'_0(T_2 - T_1)} \quad (3)$$

Combining Eqs. (1)–(3), one can easily obtain for the true TEC ($\bar{\alpha}_T$)

$$\bar{\alpha}_T = \frac{\bar{\alpha} \cdot \Delta T - \gamma \cdot \Delta\delta}{(\gamma \cdot \Delta\delta + 1) \cdot \Delta T} \quad (4)$$

where $\gamma = (\epsilon_C/\Delta\delta)$. The average $\bar{\alpha}_T$ values at 920–1150 K, estimated in such a manner, are listed in Table 4. In spite of large errors associated with the limited number of experimental data points and use of linear approximation

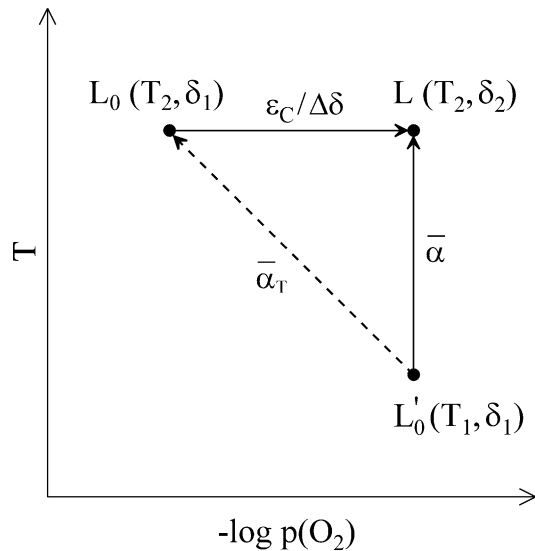


Fig. 10. Schematic illustration of the length variations on heating, explaining the suggested correction of the apparent thermal expansion coefficient for the chemical expansion due to oxygen losses.

models, the estimates of $\bar{\alpha}_T$ in air are quite close to TECs in the low-temperature range (Table 3). This suggests that the apparent increase in TEC values, observed on heating at a fixed oxygen pressure (Fig. 3), is mainly due to the chemical strain. Also, it should be mentioned that, except for the data at $p(\text{O}_2) = 1 \times 10^{-4}$ atm, the $\bar{\alpha}_T$ values increase when the gallium content increases or the oxygen pressure decreases. This behavior may be ascribed to the correlation between lattice expansion and oxygen vacancy concentration, similar to the $(\epsilon_C/\Delta\delta)$ parameter.

Summarizing the earlier discussion, Fig. 11 compares oxygen nonstoichiometry dependencies of the TECs, corrected for the chemical strain on heating, the $(\epsilon_C/\Delta\delta)$ coefficient, and the oxygen ionic conductivity of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics in air.^{17,18} Notice that due to surface exchange-affected oxygen permeability and faradaic efficiency of $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$ membranes, the apparent ionic conductivity of the undoped ferrite is slightly lower than the true values; on the contrary, no surface effect was found for the two Ga-containing

Table 4

Thermal expansion coefficients of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics in different atmospheres at 920–1150 K, corrected for the chemical expansion due to oxygen loss in the course of heating at constant $p(\text{O}_2)$

x	$p(\text{O}_2)$, atm	$\bar{\alpha}_T \times 10^6, \text{K}^{-1}$
0	1.0	9.8
	0.21	11.7
	1×10^{-4}	26.3
0.4	1.0	11.5
	0.21	13.8
	1×10^{-4}	22.5

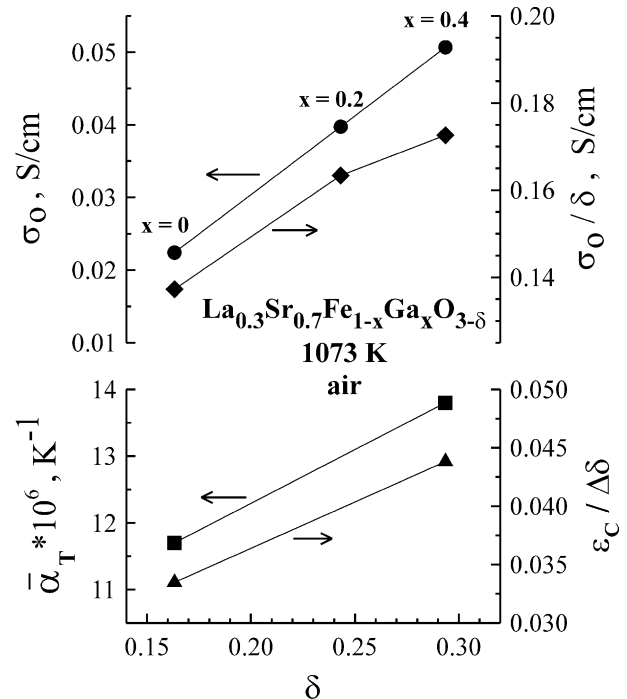


Fig. 11. Oxygen nonstoichiometry dependence of the ionic conductivity, σ_o/δ ratio, corrected TECs and $(\epsilon_C/\Delta\delta)$ parameter in the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ system at 1073 K in air.

compositions.¹⁷ The coefficients $\bar{\alpha}_T$ and $(\epsilon_C/\Delta\delta)$ both increase with increasing oxygen deficiency when x increases. Similar tendencies are found for the ionic conductivity (σ_o) and the ratio σ_o/δ . As oxygen transport in perovskites occurs via the vacancy mechanism, the latter quantity is proportional to the oxygen vacancy mobility and in theory should be independent or slightly decrease with increasing δ due to lower concentration of sites available for the vacancy jumps.³⁵ Increasing σ_o/δ ratio with δ indicates, hence, energetic facilitation of ionic conduction when gallium is incorporated into the B sites.

The correlations between ion diffusivity and thermal expansion are well known;^{21,22,25,29,31} the phenomenological theory of ionic conduction³⁵ explains them by decreasing interaction of ions in the lattice as the crystal expands. One analogous explanation is applicable to the correlation between chemical strain and ionic conductivity (Fig. 11). The observed increase in the vacancy mobility, thermal expansion and $\epsilon_C/\Delta\delta$ coefficient with increasing δ might also be attributed to a decrease in the binding energy of perovskite phases, resulting from greater vacancy concentration.²⁴ At the same time, one should briefly mention that all these correlations, including the increase in δ with x , reflect the changes in thermodynamic properties of lanthanum-strontium ferrite, which occur on Ga doping. Substitution of iron for gallium was shown to affect the equilibrium of the perovskites with the gas phase, making oxygen incorporation energetically less favorable.¹⁹

Finally, both the apparent thermal expansion in atmospheres with a fixed oxygen pressure and the isothermal chemically-induced strain of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ceramics are found to decrease with Ga additions. This enhances the stability of these materials under the oxygen-membrane operating conditions. However, the thermal expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ is still very high, limiting the compatibility of Ga-doped ferrites with other materials of electrochemical cells at elevated temperatures. In comparison with other mixed conductors promising for membrane applications, such as $\text{La}(\text{Ga},\text{Ni})\text{O}_{3-\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ -based solid solutions,^{23,31} the TECs of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ are 50–100% higher. Taking into account the results²⁸ showing that chemically-induced stresses in tubular- and planar-type membranes are similar, one can suggest that the tubular-type membrane geometry with hermetization in a low-temperature zone is preferable for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ ceramics. The use of these materials in planar-type membranes, sealed at high temperatures, seems problematic.

4. Conclusions

The linear thermal expansion coefficients of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0\text{--}0.4$) ceramics in air, determined by the dilatometric and high-temperature XRD measurements, vary in the range $(11.6\text{--}13.0)\times 10^{-6}\text{ K}^{-1}$ at 300–770 K and $(21.4\text{--}25.2)\times 10^{-6}\text{ K}^{-1}$ at 770–1170 K, decreasing with gallium content. The drastic increase in TECs at 700–800 K was found to be mainly apparent, resulting from chemically-induced expansion of the lattice due to oxygen loss on heating. At oxygen partial pressures from 10^{-4} to 1 atm, the chemical strain is a linear function of the oxygen nonstoichiometry variations. The coefficient ($\varepsilon_C/\Delta\delta$), a quantitative measure of the chemically-induced expansion, varies for $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ in the range $(1.7\text{--}5.9)\times 10^{-2}$ and follows an Arrhenius-type temperature dependence at 920–1150 K. The TEC values, corrected for the chemical strain on heating, are close to TECs at low temperatures. Both thermal and chemical expansion coefficients were shown to increase with gallium additions. As for the increase in TECs with reducing oxygen pressure, this behavior is associated with greater oxygen nonstoichiometry of Ga-containing materials.

Doping with gallium decreases the apparent thermal expansion of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ at fixed oxygen pressures and suppresses total chemical strain of the ceramics due to decreasing oxygen nonstoichiometry variations. In comparison with other group of mixed-conducting membrane materials, perovskite-like $\text{Sr}(\text{Fe},\text{Co})\text{O}_{3-\delta}$, the chemical strain in $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}(\text{Ga})\text{O}_{3-\delta}$ perovskites is significantly lower. However,

both thermal and chemical expansion coefficients of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_{3-\delta}$ ceramics are still high, which makes the tubular-type membrane geometry preferable for these mixed conductors.

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