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Electrical Conductivity and Thermodynamic Properties of Some Alkaline Earth-Doped Lanthanum Chromites[1]

S. Tanasescu,[2,3] A. Orasanu,[2,4] D. Berger,[5] I. Jitaru,[5] and J. Schoonman[6]

Alkaline-earth doped lanthanum chromites are currently the interconnecting materials of choice for solid oxide fuel cells (SOFCs). Since these materials in SOFC operating conditions are under a large oxygen potential gradient and at high temperature (1273 K), a thorough knowledge of their physical and thermochemical properties is very important. In the present study, the alkaline-earth doped lanthanum chromites $La_{1-x}Sr_xCrO_3$ ($x = 0$–0.3) and $La_{0.7}Ca_{0.3}CrO_3$ were prepared from complex precursors isolated from the $La(NO_3)_3$–$Cr(NO_3)_3$–urea system. The oxide powders were characterized by means of X-ray diffraction (XRD). The DC electrical conductivities of the samples were measured in the temperature range of 295–1273 K in air. The thermodynamic properties represented by the relative partial molar free energies, enthalpies, and entropies of oxygen dissolution in the perovskite phase, as well as the partial pressures of oxygen, have been investigated by the solid electrolyte galvanic cells method coupled with the solid-state coulometric titration technique, within the temperature range of 1073–1273 K and in a reducing atmosphere (10^{-5} Pa). The variation of the electrical conductivities and thermodynamic properties with changing oxygen stoichiometry is discussed. The study demonstrates new correlations existing between the structural, electrical, and thermodynamic properties in the doped lanthanum chromites.

KEY WORDS: doped lanthanum chromites; electrical conductivity; point defect equilibrium; thermodynamic properties.

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[2] Institute of Physical Chemistry, Laboratory of Chemical Thermodynamics, Splaiul Independentei 202, 060041 Bucharest, Romania.

[3] To whom correspondence should be addressed. E-mail: stanasescu@chimfiz.icf.ro

[4] Present address: Advanced Materials Surfaces and Interfaces Research Centre, The Robert Gordon University, St. Andrew Street, Aberdeen AB25 1HG, United Kingdom.

[5] "Politehnica" University Bucharest, Department of Inorganic Chemistry, 1 Polizu street, 78126-Bucharest, Romania.

[6] Delft University of Technology, Laboratory for Inorganic Chemistry, Julianalaan 136, 2628 BL Delft, The Netherlands.

1. INTRODUCTION

The interconnect material for solid oxide fuel cells (SOFCs) requires high chemical stability and compatibility with contacting electrode materials from room temperature up to the operating temperature, high electronic conductivity and negligible ionic conductivity in both oxygen and hydrogen atmospheres, high density to prevent cross leakage of fuel and oxidant gases, a thermal expansion coefficient (TEC) matched with the electrode materials, and minimal volatilization losses [1, 2].

To improve these properties, a great amount of work was performed involving the preparation, structural studies, and physical properties (e.g., electrical conductivity) and their relationships. However, there has been only limited information on the thermodynamic behavior in both oxidizing and reducing atmospheres, as well as on the relationships correlations existing between the electrical and thermodynamic properties when the materials are used under a large potential gradient and at high temperature (1273 K) [3–6].

In this study, we have investigated the electrical conductivity and the thermodynamic properties of $La_{1-x}Sr_xCrO_3$ ($x = 0.1 - 0.3$) and $La_{0.7}Ca_{0.3}$ CrO_3 substituted lanthanum chromites. The electrical conductivities are measured in air as a function of composition and temperature within the temperature range of 295–1273 K. In order to demonstrate the change of the charge compensation mechanism under a reducing atmosphere, thermodynamic properties represented by the relative partial molar free energies, enthalpies, and entropies of oxygen dissolution in the perovskite-phase, as well as the equilibrium partial pressures of oxygen, have been obtained as a function of temperature and substituent nature within the temperature range of 1073–1273 K and in a reducing atmosphere (10^{-5} Pa). The effect of the oxygen stoichiometry change on the thermodynamic properties was examined using the data obtained by a solid-state coulometric titration technique coupled with electromotive force measurements. For the non-stoichiometric compositions, the electrical conductivities were calculated and the results are discussed in relationship with the defect chemical equilibrium. The research was focused on emphasizing the electrical and thermodynamic behavior at low changes of oxygen stoichiometry, a topic for which there is insufficient data reported in the literature.

2. EXPERIMENTAL

The undoped and alkaline-earth (Sr- and Ca-) metal-doped lanthanum chromites were prepared by pyrolysis of the urea-containing precursors. The complex precursors were obtained in aqueous solution from metal nitrates and urea, at molar ratios of La:Cr:M(II): $CO(NH_2)_2 = (1-x):1:x:5$ (M = Sr, Ca; $x = 0-0.3$). Stoichiometric amounts of high purity metal nitrates (Merck) were dissolved in a minimum volume of deionized water. A saturated aqueous solution of urea (Riedel-de Haën) was added with stirring to the aqueous solution of corresponding metal nitrates. Then, the mixture was heated at $\sim 383\,K$ on a hot plate with stirring to evaporate the water until a green precipitate was obtained. The precursor was washed with ether and dried in air. The alkaline-earth metal-doped lanthanum chromites, $La_{1-x}M_xCrO_3$ (M = Ca, Sr), were prepared by calcining of the corresponding complex precursors at 1273 K, 2 h (for $x = 0.1; 0.2$) and 1473 K, 2 h ($x = 0.3$) in air. The undoped lanthanum chromite was obtained by calcining at 1073 K, 0.5 h. The powders were investigated by X-ray diffraction (XRD). XRD patterns were obtained using a Bruker AXS D8 Advance diffractometer with CuK_α radiation at a step of 0.02° per second in the range $2\theta = 10$ to 90°. The ceramic specimens were obtained by pressing the single-phase powders into pellets at $3 \times 10^{-6}\,kg \cdot cm^{-2}$ and sintering at 1623 K for 10 h in air. The relative density of the sintered pellets was determined by the standard Archimedes method, and the values are larger than 92% for each composition.

The DC electrical conductivity of the doped lanthanum chromite samples was measured by means of the standard four-probe technique in the temperature range of 295–1273 K in air. The pellets (10 mm diameter, 2 mm thick) were placed in an alumina tube. Platinum meshes with four platinum terminals were attached to the pellet. The electrical conductivity cell was tightened by springs to decrease the contact electrical resistance. A Pt–PtRh thermocouple was used to measure the temperature in the cell.

The solid-oxide electrolyte galvanic cells method was employed to obtain the thermodynamic properties of the samples. The electromotive force measurements were performed in the 1073–1273 K temperature range on galvanic cells incorporating $ZrO_2(Y_2O_3)$ solid electrolyte and an iron-wüstite reference electrode. The measurements were carried out in vacuum at a residual gas pressure of 10^{-5} Pa. The design of the apparatus, as well as the theoretical and experimental considerations related to the applied method, are described elsewhere [7]. The electromotive force was measured with a Keithley 197 microvoltmeter at 50 K intervals, each time waiting until equilibrium values are recorded. The determinations were considered as being satisfactory when values for increasing and decreasing temperature agreed within 1 or 2 mV.

After the measurements were completed over a range of temperatures, at a constant composition, oxygen was removed from the sample by solid-state coulometric titration [7] using a Bi-PAD Tacussel potentiostat. The titrations were performed *in situ* at 1123 K at a pressure of 10^{-5} Pa. According to Faraday's law, the mass change $|\Delta m|$ (g) of the sample is related to the transferred charge Q(A·s) by

$$|\Delta m| = 8.291 \times 10^{-5} Q \tag{1}$$

After the desired amount of electricity was passed through the cell, the current circuit was opened and sufficient time (about 3 h) had to be allowed for the electrode to equilibrate. Practically, we considered that EMF had reached its equilibrium value when three subsequent readings at 30 min intervals varied by less than 0.5 mV. After the sample reached equilibrium, for every newly obtained composition, the temperature was changed under open-circuit condition, and the equilibrium EMFs for different temperatures between 1073 and 1273 K were recorded.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the pure and alkaline-earth doped lanthanum chromites were all identified as belonging to the orthorhombic perovskite-type structure. Unit cell parameters are presented in Table I.

By comparing the unit cell volume values, it is noted that the relative increase in the unit cell volume due to the substitution of La^{3+} by Sr^{2+} ($r_{La^{3+}} = 1.23$ Å, $r_{Sr^{2+}} = 1.25$ Å in dodecahedral coordination [8]) is compensated by the formation of higher valence state chromium ions ($r_{Cr^{3+}} = 0.69$ Å and $r_{Cr^{4+}} = 0.60$ Å in octahedral coordination), which leads to the lattice contraction. More significant is the unit cell volume decrease in the case of the presence of Ca^{2+} ions ($r_{Ca^{2+}} = 1.07$ Å) (Table I).

Figure 1 shows the temperature dependence of the electrical conductivity measured for $La_{1-x}M_xCrO_3$ with different doping ion contents in air. The literature data for pure lanthanum chromite are shown for comparison [9, 10]. The conduction mechanism of alkaline-earth doped

Table I. Unit Cell Parameters of Pure and Doped Lanthanum Chromite Samples

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)
$LaCrO_3$	5.5024	5.4849	7.7520	233.96
$La_{0.9}Sr_{0.1}CrO_3$	5.4954	5.4718	7.7472	232.95
$La_{0.8}Sr_{0.2}CrO_3$	5.5091	5.4125	7.7716	231.73
$La_{0.7}Sr_{0.3}CrO_3$	5.4638	5.4712	7.7602	231.98
$La_{0.7}Ca_{0.3}CrO_3$	5.4490	5.4386	7.6636	227.11

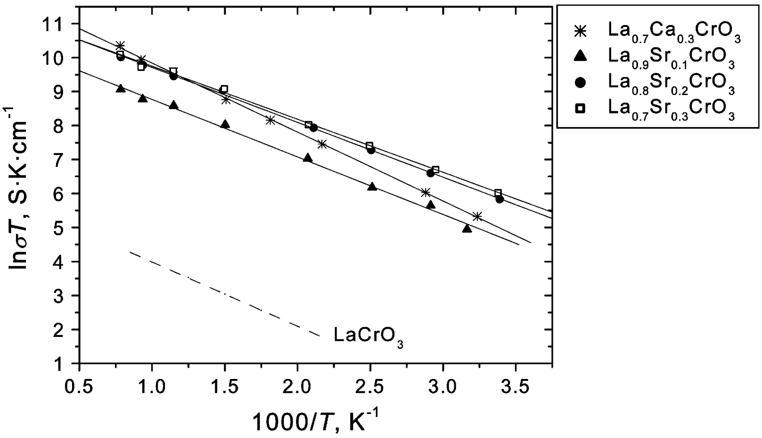

Fig. 1. Temperature dependence of the electrical conductivity of $La_{1-x}M_xCrO_3$ in air. The data for $LaCrO_3$ (the dotted line) are taken from Ref. [9].

lanthanum chromites in air is electron hopping between Cr^{3+} to Cr^{4+} ions. At high oxygen pressure the divalent doping is electronically compensated by Cr^{4+} [4, 11]. The electrical conductivity in air is well represented by the relationship $\sigma = (\sigma_o/T)\exp(-E/(kT))$ (where σ is the electrical conductivity, σ_o is the pre-exponential factor, T is the absolute temperature, k is Boltzmann's constant, and E is the activation energy of conduction) which was generally used for the hopping small-polaron model. The activation energy of all samples calculated from the slopes of the least-squares fit of $\ln(\sigma T)$ vs. $(1000/T)$ and the correlation coefficients, R, are listed in Table II.

For doped lanthanum chromites the conductivity increases with an increase of the acceptor dopant content. The electrical conductivity and the activation energy values of the $La_{0.7}Ca_{0.3}CrO_3$ at high temperature ($T > 1073$ K) are higher than the values obtained for the Sr-doped com-

Table II. Activation Energy of Conduction and Correlation Coefficient

Sample	E (kJ · mol^{-1})	R
$La_{0.9}Sr_{0.1}CrO_3$	14.1	0.9977
$La_{0.8}Sr_{0.2}CrO_3$	13.4	0.9995
$La_{0.7}Sr_{0.3}CrO_3$	13.0	0.9987
$La_{0.7}Ca_{0.3}CrO_3$	16.9	0.9997

pounds (Table II). This finding is in close agreement with the literature data for Ca- and Sr-doped materials [12].

In order to get a better understanding of the long-time stability of perovskite-type solutions based on lanthanum chromites, investigations from a thermodynamic point of view are very important. Moreover, few experimental data are available in the literature. The materials based on lanthanum chromites are used at high temperatures and in drastic oxygen potential gradients. According to previous studies [4], at temperatures around 1273 K, 10^{-5} Pa is a limiting pressure, under which the charge imbalance caused by the introduction of dopant starts to be compensated by the formation of oxygen vacancies. Consequently, our research was focused on emphasizing the thermodynamic behavior at this critical pressure (10^{-5} Pa) and within the temperature range of 1073–1273 K in order to obtain the thermodynamic values from which the ionic charge compensation can be deduced.

As we showed in previous papers [13, 14], the thermodynamic stability limits of the doped lanthanum chromites are conveniently situated within the range of oxygen chemical potentials which can be measured using galvanic cells of the type:

$$(-)\mathrm{Fe,\ w\ddot{u}stite/ZrO_2(Y_2O_3)/ABO_3}(+) \tag{1}$$

where, for simplicity, we de-noted a lanthanum perovskite-type oxide with ABO_3.

Since the electrolyte of the cell shows only ionic conduction due to migration of oxygen ions in the electrolyte, the virtual cell reaction may be expressed in terms of oxygen transfer from the right-hand to the left-hand electrode. Hence, the EMF of the cell is

$$E = \frac{\mu_{O_2} - \mu_{O_{2(\mathrm{ref})}}}{4F} \tag{2}$$

where μ_{O_2} and $\mu_{O_{2(\mathrm{ref})}}$ are, respectively, the oxygen chemical potentials of the perovskite and the reference electrode, and F is the Faraday constant. With a knowledge of the free energy change of the reference electrode reaction evaluated from calorimetrically verified gas equilibrium measurements [15–17],

$$\Delta G^0_{\mathrm{Fe,\ w\ddot{u}stite}} = [-264.575 + 0.065T]\ \mathrm{kJ \cdot mol^{-1}} \tag{3}$$

and upon substituting the experimental values of E in Eq. (2), the values of the relative partial molar free energy of the solution of oxygen in the perovskite phase and hence the pressures of oxygen in equilibrium with the solid can be calculated;

$$\Delta\overline{G}_{O_2} = RT \ln P_{O_2} \tag{4}$$

The relative partial molar enthalpies and entropies were obtained according to the known relationships:

$$\frac{\partial \frac{\Delta \overline{G}_{O_2}}{T}}{\partial T} = -\frac{\Delta \overline{H}_{O_2}}{T^2} \tag{5}$$

$$\Delta \overline{G}_{O_2} = \Delta \overline{H}_{O_2} - T \Delta \overline{S}_{O_2} \tag{6}$$

The overall uncertainty due to the temperature and potential measurement (taking into account the overall uncertainty of a single measurement and also the quoted accuracy of the voltmeter) was ±1.5 mV. This was equivalent to ±0.579 kJ·mol^{-1} for the free energy change of the cell. Considering the uncertainty (±0.523 kJ·mol^{-1}) in the thermodynamic data for the iron-wüstite references [16, 17], the overall uncertainty of the data was thus estimated to be 1.6 kJ·mol^{-1}. For the enthalpies the error was ±0.45 kJ·mol^{-1} and for the entropies ±1.1 J·mol^{-1}·K^{-1}. Errors due to the data taken from the literature are not included in these values because of the unavailability of reliable standard deviations. The obtained results are listed in Table III and plotted in Figs. 2 and 3.

In the temperature range of 1073–1273 K, the partial molar free energy is a linear function of temperature. The partial molar entropies and enthalpies are independent of temperature in this temperature range. One can observe that, at the same concentration of the A-site dopant (30%), the $\Delta \overline{G}_{O_2}$ and log P_{O_2} values increase for the lanthanum strontium chromite compared with the values obtained for the Ca-doped compound (Figs. 3 and 4), while the $\Delta \overline{S}_{O_2}$ decreases to a more negative value. This observation indicated that under the respective work condition the charge imbalance caused by A-site doping is compensated by the formation of oxygen vacancies. As one can see from Table III, the partial molar

Table III. Relative Partial Molar Thermodynamic Data of Oxygen in the Substituted Compounds (1073–1273 K)

	$\Delta \bar{G}_{O_2} = \Delta \bar{H}_{O_2} - T \Delta \bar{S}_{O_2}$	
Sample	$\Delta \bar{H}_{O_2}$ (kJ · mol^{-1})	$\Delta \bar{S}_{O_2}$ (kJ · mol^{-1} · K^{-1})
$La_{0.9}Sr_{0.1}CrO_3$	−598.731 ± 15.1	−0.185 ± 0.01
$La_{0.8}Sr_{0.2}CrO_3$	−670.573 ± 2.8	−0.287 ± 0.00
$La_{0.7}Sr_{0.3}CrO_3$	−662.744 ± 9.5	−0.396 ± 0.01
$La_{0.7}Ca_{0.3}CrO_3$	−575.389 ± 8.3	−0.228 ± 0.01

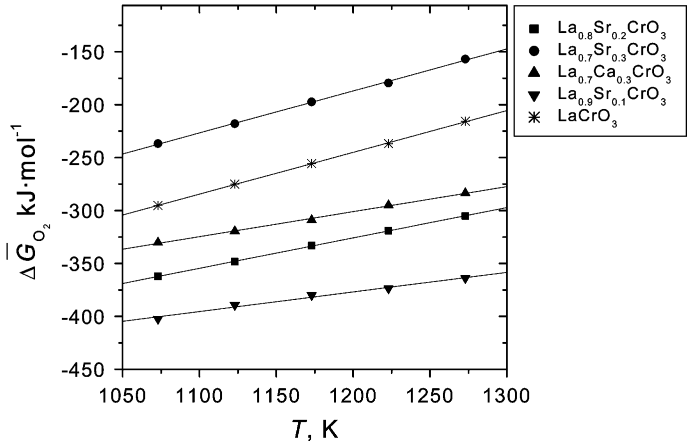

Fig. 2. Variation of $\Delta\overline{G}_{O_2}$ with temperature for the substituted and unsubstituted $LaCrO_3$.

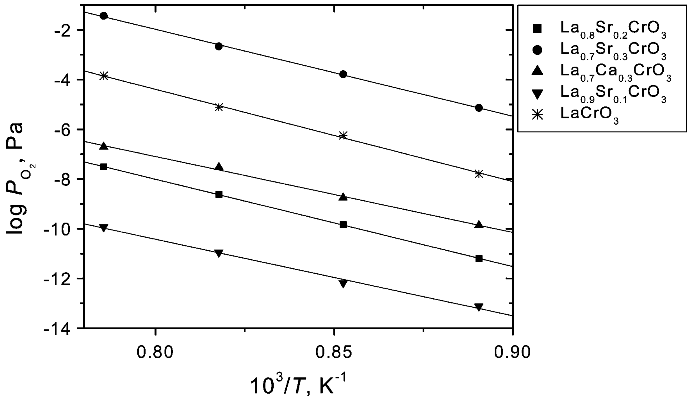

Fig. 3. Plot of $\log p_{O_2}$ vs. $1/T$ for the substituted and unsubstituted $LaCrO_3$.

enthalpy is strongly dependent upon the cation size for the same temperature range. $\Delta\overline{H}_{O_2}$ is smaller for the Ca-doped than for the Sr-doped chromite.

Comparing the data obtained for samples with different Sr content, one can observe that the $\Delta\overline{G}_{O_2}$ values increase correspondingly with increasing x, suggesting that oxygen vacancies can be easily formed when the Sr concentration is high. In addition, the log P_{O_2} values increase towards the lanthanum strontium chromite with higher strontium content. A strong dependence of the thermodynamic data on the Sr-content of

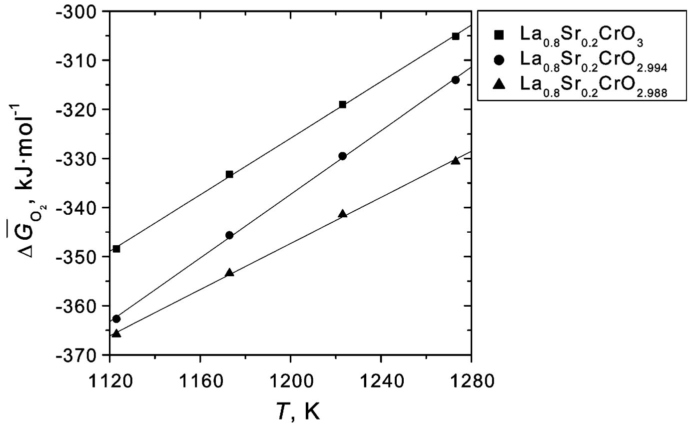

Fig. 4. $\Delta\overline{G}_{O_2}$ variation with temperature for the compound $La_{0.8}Sr_{0.2}CrO_3$ before and after two successive titrations.

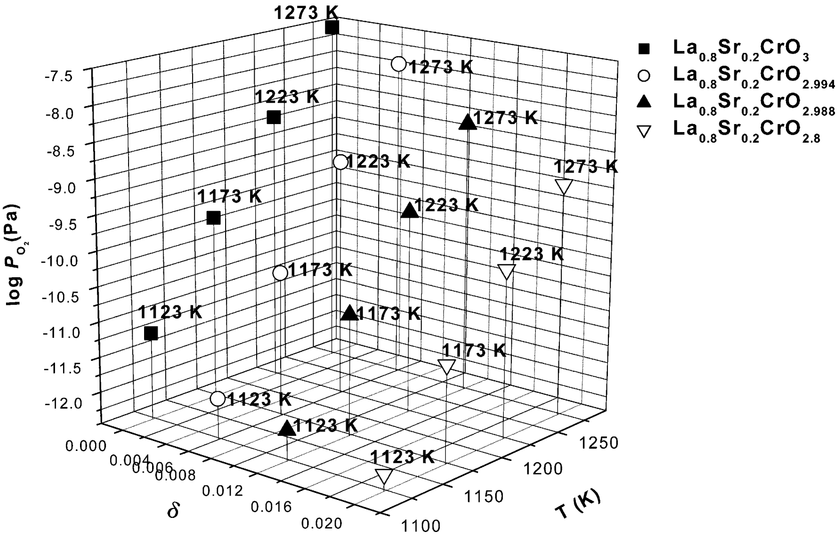

Fig. 5. $\log p_{O_2}$ variation with temperature and oxygen nonstoichiometry for the compound $La_{0.8}Sr_{0.2}CrO_{3-\delta}(0 < \delta < 0.02)$.

the doped lanthanum chromite perovskites was also noticed by Mizusaki et al. [3] in the temperature range of 1273–1573 K. They suggested that the strontium on the La site causes not only the valence control effect, but also the strong interactions with the oxygen sublattice.

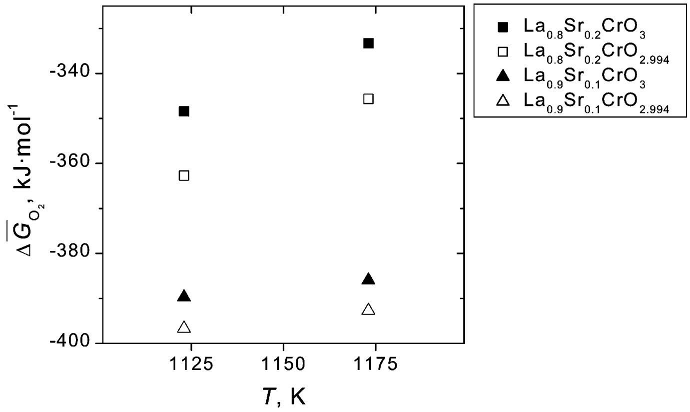

Fig. 6. Variation of $\Delta\overline{G}_{O_2}$ with temperature before and after titration for $La_{1-x}Sr_xCrO_{3-\delta}$ ($x = 0.1$; 0.2; $\delta = 0.006$).

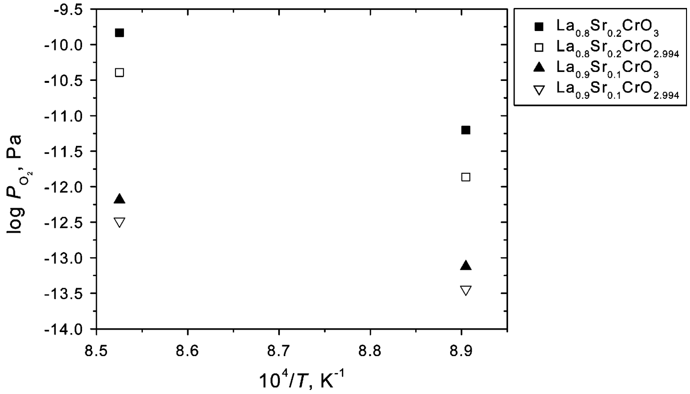

Fig. 7. Variation of $\log p_{O_2}$ with temperature before and after titration for $La_{1-x}Sr_xCrO_{3-\delta}$ ($x = 0.1$; 0.2; $\delta = 0.006$).

The thermodynamic behavior at small changes of oxygen stoichiometry (with δ ranging from 0.006 to 0.02) has been demonstrated by measurements on $La_{0.8}Sr_{0.2}CrO_3$ and $La_{0.9}Sr_{0.1}CrO_3$ samples (Figs. 4–7).

The variation of $\Delta\overline{G}_{O_2}$ with temperature before and after two successive titrations for the composition with $x = 0.2$ is shown in Fig. 4. One can observe the decrease of the $\Delta\overline{G}_{O_2}$ values after titration. It is interesting to note that for the stoichiometry change from $\delta = 0.006$ to $\delta = 0.012$, the partial molar entropy values increase by 89 J·mol^{-1}·K^{-1}, suggesting an increase of order in the oxygen sublattice.

For the same composition with $x = 0.2$, the variation of $\log P_{O_2}$ with $\delta (0 < \delta < 0.02)$ is shown in Fig. 5. A decrease of $\log P_{O_2}$ with δ is observed. At the same deviation of the oxygen stoichiometry, the partial pressures of oxygen increase with temperature.

The variation of the thermodynamic data with the stoichiometry change and the concentration of the dopant have been evidenced by measurements at 1123 and 1173 K on $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ and $La_{0.1}Sr_{0.1}CrO_{3-\delta}$ with $\delta = 0.006$ (Figs. 6 and 7). It is noted that the $\Delta \overline{G}_{O_2}$ and $\log P_{O_2}$ values decrease after titration for both compounds and, at the same deviation of the oxygen stoichiometry ($\Delta\delta = 0.006$), the energy values increase with temperature. The obtained results confirm that in reducing environment (10^{-5} Pa) and at temperatures of 1073–1273 K, oxygen vacancies are generated at the expense of electron holes. The charge imbalance caused by the introduction of Sr starts to be compensated by the formation of oxygen vacancies.

A correlation between the defect equilibrium in $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ and the experimental data obtained in this work is discussed in the following. Considering the defect model treated in previous studies [3, 4, 18] and using the Kröger–Vink notation [19], the dissolution reaction of oxygen into the sample with $x = 0.2$ can be expressed by

$$1/2O_2 + V_O^{\bullet\bullet} + 2Cr_{Cr}^{x} = O_O^{x} + 2Cr_{Cr}^{\bullet} \tag{7}$$

and the equilibrium constant for this reaction is

$$K_{ox} = \frac{[Cr_{Cr}^{\bullet}]^2[O_O^{x}]}{[Cr_{Cr}^{x}][V_O^{\bullet\bullet}]P_{O_2}^{1/2}} \tag{8}$$

where $Cr_{Cr}^{\bullet}$ is Cr^{4+} on a chromium site, O_O^{x} is a regular lattice oxide ion, Cr_{Cr}^{x} is a regular trivalent chromium ion (Cr^{3+}) in the lattice, and $V_O^{\bullet\bullet}$ is a vacancy on an oxygen site.

The neutrality condition is

$$[M'_{La}] = 2[V_O^{\bullet\bullet}] + [Cr_{Cr}^{\bullet}] \tag{9}$$

where $[M'_{La}] = x$ (the amount of divalent A-site dopant); $[V_O^{\bullet\bullet}] = \delta$; $[Cr_{Cr}^{\bullet}] = x - 2\delta$.

The equilibrium constants calculated from our experimental results were found to increase with increasing temperature (Table IV) which suggests that at higher temperatures the defect reaction (Eq. (7)) proceeds in the reverse direction to produce a significant amount of oxygen vacancies.

In order to discuss the conductivity variation in these conditions, we tentatively express K_{ox} as a function of p, the mole fraction of electron

Table IV. Hole Mobility and Equilibrium Constant Values for $La_{0.8}Sr_{0.2}CrO_{3-\delta}$

		$K_{ox}(\mathrm{Pa}^{-1/2})$		
Temperature (K)	$\mu\,(\mathrm{cm}^2 \cdot \mathrm{V}^{-1} \cdot \mathrm{s}^{-1})$	$\delta = 0.006$	$\delta = 0.012$	$\delta = 0.020$
1173	0.0311	4.20×10^6	2.63×10^6	1.56×10^6
1223	0.0321	9.20×10^5	7.02×10^6	4.90×10^5
1273	0.0323	2.34×10^5	2.18×10^5	1.42×10^5

holes. When the electronic charge carriers are transported by the small polaron hopping conduction mechanism, the charge carriers are considered to be localized at the Cr-sites and the fraction of occupied sites, p, is related to the concentration of tetravalent chromium ions. For $x = 2\delta + p$ (where $p = [\mathrm{Cr}^{\bullet}_{\mathrm{Cr}}]$), Eq. (8) can be rewritten as

$$K_{ox} = \frac{(6 - x + p)p^2}{(x - p)(1 - p)^2 P_{O_2}^{1/2}} \tag{10}$$

On the other hand, the electrical conductivity can be expressed [20, 21] as

$$\sigma = \frac{Fp\mu}{V_m} \tag{11}$$

where μ is the hole mobility, F is the Faraday constant, and V_m is the molar volume. Solving Eq. (11) for p and inserting into Eq. (10), we get

$$K_{ox} = \frac{\{(6 - x)\,\mu F + \sigma V_m\}\,(\sigma V_m)^2}{(x\mu F - \sigma V_m)\,(\mu F - \sigma V_m)^2\, P_{O_2}^{1/2}} \tag{12}$$

According to previous research [20–22] two assumptions are made: first, the mobility is independent of the hole concentration; and second, the lattice dimension does not change even the sample is in a reducing atmosphere. On the basis of these considerations, the mobility and the lattice parameter are assumed to take constant values. In these conditions, by using the equilibrium constant values and the hole mobility (Table IV) of the sample obtained from our experimental data, theoretical conductivity isotherms are calculated (Tabel V).

The electrical conductivity of the solid solution must be caused by $\mathrm{Cr}^{\bullet}_{\mathrm{Cr}}$. The obtained values are representative for the $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ sample with a small departure from stoichiometry. As expected, the oxygen vacancies start to be generated in noticeable amounts even at low δ

Table V. Comparison of Experimental Electrical Conductivity Values (σ) for $La_{0.8}Sr_{0.2}CrO_3$ in Air and Electrical Conductivities (σ_c) Calculated from the Equilibrium Constant Values for $La_{0.8}Sr_{0.2}CrO_{3-\delta}$

Temperature (K)	$\sigma(S \cdot cm^{-1})$ Experimental values for $La_{0.8}Sr_{0.2}CrO_3$ in air	$\sigma_c(S \cdot cm^{-1})$ Calculated from the equilibrium constant values of the defect reaction (7) for $La_{0.8}Sr_{0.2}CrO_{3-\delta}$		
		$\delta = 0.006$ $p = 0.188$	$\delta = 0.012$ $p = 0.176$	$\delta = 0.020$ $p = 0.160$
1173	17.66	16.59	15.52	13.71
1223	18.24	17.12	16.04	14.13
1273	18.36	17.23	16.13	14.20

and the concentration of Cr^{4+} gets smaller, resulting in the decrease in σ. This fact can be also correlated with the results of our thermodynamic study that show decreases of $\Delta\overline{G}_{O_2}$ and $\log P_{O_2}$ values with δ.

As one can see in Tabel V, at a value $\delta = 0.020$, the conductivity is almost 80% of its maximum value, in air, that is, about 20% of the negative charge by $Sr^{\bullet}_{La}$ is compensated by the formation of $V^{\bullet\bullet}_{O}$. This finding is consistent with the point defect model described by Mizusaki et al. [3] in their study of the oxygen nonstoichiometry of the Sr-doped $LaCrO_3$.

Another important characteristic is that the electrical conductivities increase with temperature, indicating thermally activated type conduction, but the conductivity values at 1223 and 1273 K are very close, indicating that the main cause of the difference in the behavior at different temperatures is the temperature dependence of the dissolution reaction of oxygen into the sample according to the reaction in Eq. (7).

4. CONCLUSIONS

Pure and alkaline-earth metal-doped lanthanum chromites were obtained by calcining of complex precursors isolated in the $La(NO_3)_3$–$Cr(NO_3)_3$–$M(NO_3)_2$–urea system. Powders of specimens were investigated by X-ray powder diffraction and were characterized as single phase with orthorhombic perovskite-like structure. The electrical conductivity in air of the doped lanthanum chromites increases with an increase in the doping ion content. The linear dependence of $\ln(\sigma T)$ vs. $1/T$ is characteristic of a small polaron hopping transport mechanism.

The solid-oxide electrolyte galvanic cell method was used to determine the thermodynamic properties of the subtituted lanthanum chromites. The influence of the strontium and calcium substituents on the thermodynamic properties are discussed related to the variation of the predominant defects in the oxygen sublattice of the perovskite structure. The obtained results confirm that in a reducing environment (10^{-5} Pa) and at temperatures of 1073–1273 K, the charge imbalance caused by the introduction of dopants starts to be compensated by the formation of oxygen vacancies.

The effect of the oxygen stoichiometry change on thermodynamic properties was examined using the data obtained by a coulometric titration technique coupled with EMFmeasurements. For oxygen stoichiometry changes with δ ranging from 0.006 to 0.02, the decrease of $\Delta\overline{G}_{O_2}$ and $\log P_{O_2}$ values with δ is observed. At the same deviation of the oxygen stoichiometry, the energy values increase with temperature. A relative stoichiometry change of $\Delta\delta = 0.006$ is followed by an increase of the partial molar entropy, suggesting an increase of order on the oxygen sublattice. For the nonstoichiometric compositions the calculated conductivity values are consistent with the point defect model described in the literature and suggest new correlations existing between the electrical, structural, and thermodynamic data.

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