

# HIGH – TEMPERATURE THERMODYNAMIC DATA OF SOME PEROVSKITE-TYPE COMPOUNDS BASED ON DOPED LANTHANUM MANGANITES AND LANTHANUM CHROMITES

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The thermodynamic properties of the lanthanum manganites and lanthanum chromites ( $ABO_3$  perovskite structure) are strongly affected not only by the A-site substituents, but also by the oxygen nonstoichiometry, as well as by the partial substitution of Mn or Cr on the B-site. It is the aim of this paper to make new measurements by using the solid electrolyte galvanic cells method in order to determine the effect of the dopants on the thermodynamic properties. The relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium oxygen partial pressures were determined as function of composition and temperature in the range of 1073÷1273 K.

## Introduction

The perovskite-type compounds based on doped and undoped lanthanum manganites and lanthanum chromites form an important and interesting object of study owing to their technologically useful electric, magnetic and catalytic properties. Besides the determination of their electrical and structural characteristics, a thorough knowledge of the thermodynamics of the new materials is very important in order to evaluate and optimize the properties for utilization in different applications such as solid oxide fuel cells and MHD electrodes, heterogeneous catalysts, colossal magnetoresistive (CMR) materials etc.

In previous papers [1÷4] we revealed that, in investigating thermodynamic properties of the perovskite-type oxides, the solid electrolyte galvanic cells technique shows large potentialities. In the present work, new measurements have been made in order to evidence the correlation between the composition and the thermodynamic properties of some perovskite-type materials of general formula  $La_{1-x}M_xMn_{1-y}M'_yO_3$  (where  $M=Ca, Sr; x=0.3; M'=Fe; y=0; 0.2; 0.7$ ) and  $La_{1-x}M_xCr_{1-y}M'_yO_3$  (where  $M=Ca, Sr; x=0.1; 0.2; 0.3; M'=Mg; y=0.05$ ). The measurements are effected in the temperature range of 1073-1273 K by using a galvanic cell incorporating a  $ZrO_2(Y_2O_3)$  solid electrolyte and an iron-wüstite reference electrode. 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 obtained as a function of temperature and the dopant nature. The results are discussed being related with the variation of the predominant defects in the oxygen sublattice of the perovskite-type structure.

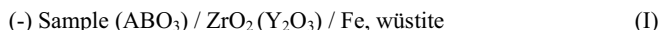
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## Experimental

The apparatus and the principal characteristics of the solid electrolyte galvanic cells were previously described [2,3].

The solid state galvanic cell employed in this study can be schematically written as follows:



The solid electrolyte is a disc of 12.84 wt% yttria stabilized zirconia (10 mm diameter, 6 mm thick) supplied by Risø National Laboratory Roskilde - Denmark.

The reference electrode is prepared from electrolytic iron (Koch-Light iron) and  $\text{Fe}_2\text{O}_3$  (Fischer Certified Reagent ferric oxide) powders mixed in a molar ratio of 4:1, pressed at 15 MPa and sintered at 1373 K in vacuum for 12 hours. Thus, small cylindrical pieces 2 mm thick and 2 mm high were prepared.

The compositions of the samples are listed in Table 1.

The powder of the alkaline-earth (Sr- and Ca-) metal-doped lanthanum manganites specimens was supplied by Haldor Topsøe A/S, Lyngby, Denmark. These were prepared by drip pyrolysis and were characterized by X-ray powder diffraction as single perovskite phases [5,6]. The powders were pressed into small pellets (2 mm thick and 2 mm high) weighing 70 mg and were sintered at 1273 K in air for four hours.

The alkaline-earth (Sr- and Ca-) metal-doped lanthanum chromites were prepared by pyrolysis of the urea-containing precursors at 1273÷1473 K for 2h in air [7]. The  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$  (Praxair Speciality Chemicals) powder was supplied by Department of Materials from the Imperial College of Science, Technology and Medicine - London. The powders of doped lanthanum chromites specimens were investigated by X-ray powder diffraction and were characterized as single phases with orthorhombic perovskite-like structure. For the EMF measurements, the powders were pressed at 3000 t/cm<sup>2</sup> into pellets weighing 0.1 g and were sintered at 1623 K in air for 10 hours.

**Table 1. Composition of the specimens**

M1	$\text{La}_{0.70}\text{Sr}_{0.30}\text{MnO}_3$	S1	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$
M2	$\text{La}_{0.70}\text{Ca}_{0.30}\text{MnO}_3$	S2	$\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$
M3	$\text{La}_{0.75}\text{Sr}_{0.30}\text{Mn}_{0.80}\text{Fe}_{0.20}\text{O}_3$	S3	$\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$
M4	$\text{La}_{0.75}\text{Sr}_{0.30}\text{Mn}_{0.30}\text{Fe}_{0.70}\text{O}_3$	S4	$\text{La}_{0.8}\text{Sr}_{0.1}\text{CrO}_3$
		S5	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.95}\text{Mg}_{0.05}\text{O}_3$

The measurements are performed in vacuum at a residual gas pressure of  $10^{-6}$  Pa. The EMF measurements were undertaken with an accuracy of 1 mV by means of a Keithley 197 Microvoltmeter. The electromotive force was measured at increasing and decreasing temperature, within the 1073÷1273 K range. The readings were made at 50 K intervals, every time waiting till the equilibrium values were recorded. The determinations were considered to be satisfactory, when values for increasing and decreasing temperatures agreed within 1 or 2 mV. The potential was measured with the furnace on, since tests have shown that the variation of potential on switching off the furnace was only 0.05 mV.

## Results and discussion

Since the solid electrolyte of the cell is a purely anionic conductor, the voltage for the cell (I) is a measure of the difference in oxygen chemical potential of the sample and of the equilibrium mixture of iron and wüstite. The free energy change of the cell is given by the expression:

$$\Delta G_{\text{cell}} = \mu_{\text{O}_2} - \mu_{\text{O}_{2(\text{ref})}} = 4FE \quad (1)$$

where  $E$  is the cell electromotive force in volts;  $\mu_{\text{O}_2}$ ,  $\mu_{\text{O}_{2(\text{ref})}}$  are the oxygen chemical potentials of the perovskite and the reference electrode, respectively and  $F$  is the Faraday constant ( $F = 96.508 \text{ kJ/V equiv.}$ ). Upon substituting the experimental values of  $E$  in equation (1) and knowing the free energy change of the reference electrode evaluated from calorimetrically verified gas equilibrium measurements [8÷10], the values of the relative partial molar free energy of oxygen dissolution in the perovskite phase and hence the pressures of oxygen in equilibrium with the solid can be calculated:

$$\Delta \bar{G}_{\text{O}_2} = RT \ln p_{\text{O}_2} \quad (2)$$

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

$$\frac{\partial \frac{\Delta \bar{G}_{\text{O}_2}}{T}}{\partial T} = - \frac{\Delta \bar{H}_{\text{O}_2}}{T^2} \quad (3)$$

$$\Delta \bar{G}_{\text{O}_2} = \Delta \bar{H}_{\text{O}_2} - T \Delta \bar{S}_{\text{O}_2} \quad (4)$$

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  $\pm 1.5 \text{ mV}$ . This was equivalent to  $\pm 0.579 \text{ kJ mol}^{-1}$  for the free energy change of the cell. Considering the uncertainty  $\pm 0.523 \text{ kJ mol}^{-1}$  in the thermodynamic data for the iron-wüstite references [9,10], the overall accuracy of the data was estimated to be  $1.6 \text{ kJ mol}^{-1}$ . For the enthalpies the errors were  $\pm 0.45 \text{ kJ mol}^{-1}$  and for the entropies  $\pm 1.1 \text{ J mol}^{-1} \text{ K}^{-1}$ .

The obtained results are plotted in Figs. 1÷4 and listed in Table 2.

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 a previous paper [1] was shown that the effect of Sr-doping in lanthanum manganites is seen to be an increase of  $\Delta \bar{G}_{\text{O}_2}$  and  $\log p_{\text{O}_2}$ , while the relative partial molar entropy is decreased to a more negative value. This observation can be explained by the increase of the oxygen vacancies concentration when  $\text{La}^{3+}$  ions are replaced by  $\text{Sr}^{2+}$  ions.

At the same concentration of the A-site dopant (30%), the  $\Delta \bar{G}_{\text{O}_2}$  and  $\log p_{\text{O}_2}$  values increase for the lanthanum strontium manganite comparatively with the values obtained for the Ca-doped compound (Figs. 1 and 2).

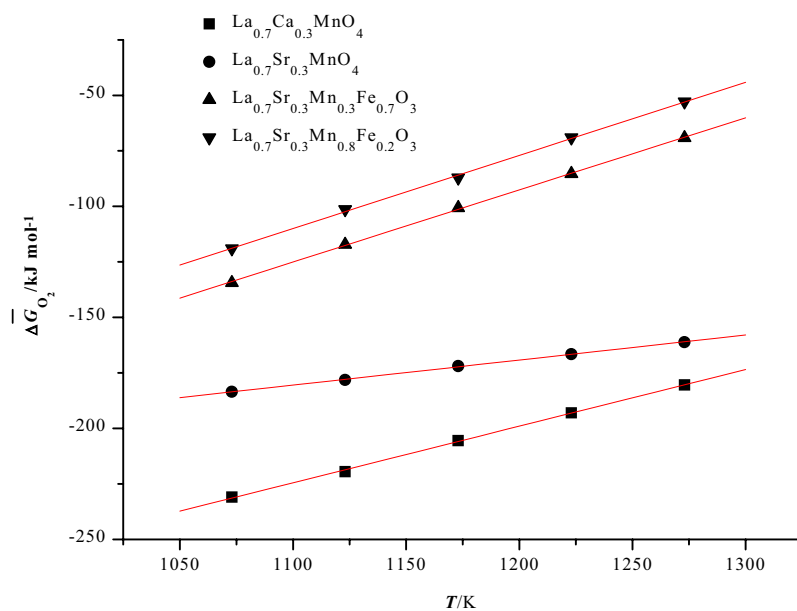


Fig. 1: The variation of  $\Delta\bar{G}_{\text{O}_2}$  with temperature.

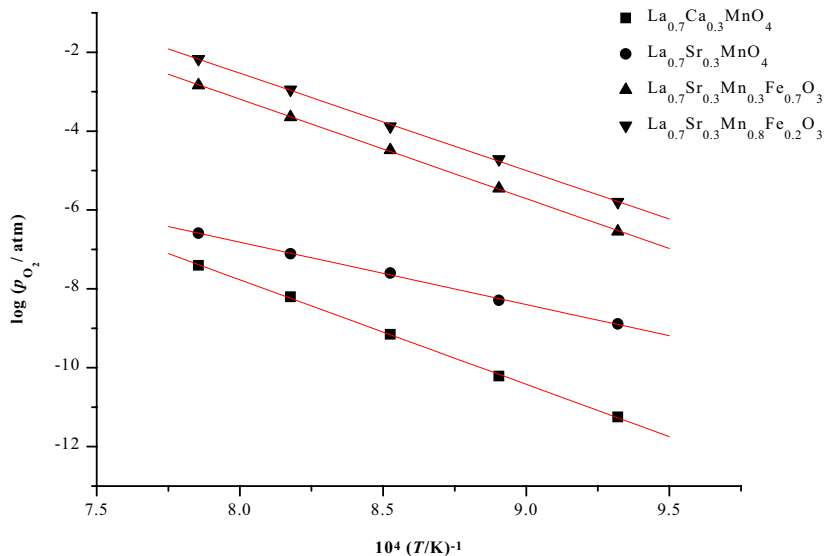


Fig. 2: The plot of  $\log p_{\text{O}_2}$  versus  $1/T$ .

As one can see from the Table 2, for the same temperature range, the partial molar enthalpy and entropy are strongly dependent upon cation size. For the Sr-doped compound, higher values of  $\Delta\bar{H}_{O_2}$  and  $\Delta\bar{S}_{O_2}$  (Table 2) are obtained, suggesting that the  $Sr^{2+}$  ions can hold the perovskite-structure more effectively comparatively with the  $Ca^{2+}$  ions; that is the oxygen vacancies are easily formed in the strontium doped lanthanum manganites than in the analogous calcium ones. This statement agrees with the conclusions of Yokokawa and co-workers [11] who estimated the thermodynamic properties of some lanthanum transition metal perovskites using an empirical correlation between the stabilization energy and the valence stability. So, when the vacancy formation should be avoided on doping of alkaline earths, calcium will be appropriate as dopant, whereas strontium doping may act as an oxide ion vacancy producer.

As one can see from the Table 2 and Figs. 1 and 2, the group of lanthanum strontium ferrite manganites is very well made distinct by their thermodynamic data and the obtained results can be discussed only being related to the effect of the iron content.

The  $\Delta\bar{G}_{O_2}$  values increase correspondingly for the compounds in which iron is present. Regarding the partial molar heats of solution, they are comparatively higher in lanthanum strontium ferrite manganites than in lanthanum strontium manganites with the same strontium content, suggesting that the predominant defects are different in the two groups of compounds. All these findings can be explained by the relative redox stability of the  $B^{3+}$  ions. The  $Fe^{3+}$  ions tends to bind the  $O^{2-}$  ions more strongly than  $Mn^{3+}$  which seems to decrease (at the same A-site composition) both the mobility and the concentration of the oxygen vacancies. This statement agrees with the model suggested by Steele and co-workers [12,13] and is also confirmed by the observations of Teraoka in the study of the ionic conductivities and oxygen permeation in cobaltites doped by iron [14,15].

**Table 2: The relative partial molar thermodynamic data of oxygen in the perovskite phase (temperature range 1073÷1273)**

Compound	$\Delta\bar{G}_{O_2} = \Delta\bar{H}_{O_2} - T\Delta\bar{S}_{O_2}$	
	$\Delta\bar{H}_{O_2}$ (kJ mol <sup>-1</sup> )	$\Delta\bar{S}_{O_2}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
La <sub>0.7</sub> Sr <sub>0.3</sub> MnO <sub>3</sub>	-304.59 ± 2.1	-0.112 ± 0.001
La <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>3</sub>	-505.27 ± 4.3	-0.255 ± 0.003
La <sub>0.7</sub> Sr <sub>0.3</sub> Mn <sub>0.8</sub> Fe <sub>0.2</sub> O <sub>3</sub>	-472.05 ± 7.1	-0.329 ± 0.006
La <sub>0.7</sub> Sr <sub>0.3</sub> Mn <sub>0.3</sub> Fe <sub>0.7</sub> O <sub>3</sub>	-482.57 ± 4.5	-0.325 ± 0.004
La <sub>0.7</sub> Ca <sub>0.3</sub> CrO <sub>3</sub>	-575.389 ± 8.3	-0.228 ± 0.01
La <sub>0.9</sub> Sr <sub>0.1</sub> CrO <sub>3</sub>	-598.731 ± 15.1	-0.185 ± 0.01
La <sub>0.8</sub> Sr <sub>0.2</sub> CrO <sub>3</sub>	-670.573 ± 2.8	-0.287 ± 0.00
La <sub>0.7</sub> Sr <sub>0.3</sub> CrO <sub>3</sub>	-662.744 ± 9.5	-0.396 ± 0.01
La <sub>0.8</sub> Sr <sub>0.2</sub> Cr <sub>0.95</sub> Mg <sub>0.05</sub> O <sub>3</sub>	-658.728 ± 4.8	-0.289 ± 0.00

In the case of the doped lanthanum chromites, one can also observe that, at the same concentration of the A-site dopant (30%), the  $\Delta\bar{G}_{O_2}$  and  $\log p_{O_2}$  values increase for the lanthanum strontium chromite comparatively with the values obtained for the Ca-doped

compound (Figs. 3 and 4), while the  $\Delta\bar{S}_{O_2}$  is decreased to a more negative value (Table 2), respectively. This observation inferred that under the respective work condition the charge imbalance caused by A-site doping is compensated by the formation of oxygen vacancies (ionic charge compensation). As one can see from the Table 2, the partial molar enthalpy is strongly dependent upon cation size for the same temperature range.  $\Delta\bar{H}_{O_2}$  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  $\Delta\bar{G}_{O_2}$  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 the doped lanthanum chromite perovskites was also noticed in the temperature range of 1273÷1573 K by Mizusaki [16].

At 20% Sr, the  $\Delta\bar{G}_{O_2}$  and  $\log p_{O_2}$  values increase correspondingly for the compound in which magnesium is present. Regarding the partial molar heats of solution, they are comparatively higher for the sample containing Sr and Mg, than in lanthanum strontium chromite with the same strontium content, suggesting that the magnesium on the Cr site causes not only the valence control effect, but also the strong interactions to the oxygen sublattice.

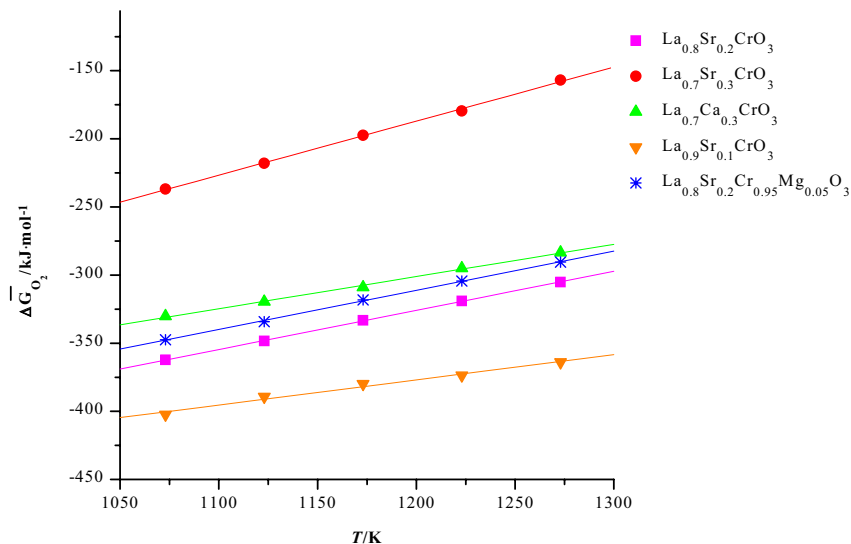


Fig. 3: The variation of  $\Delta\bar{G}_{O_2}$  with the temperature for the substituted lanthanum chromites.

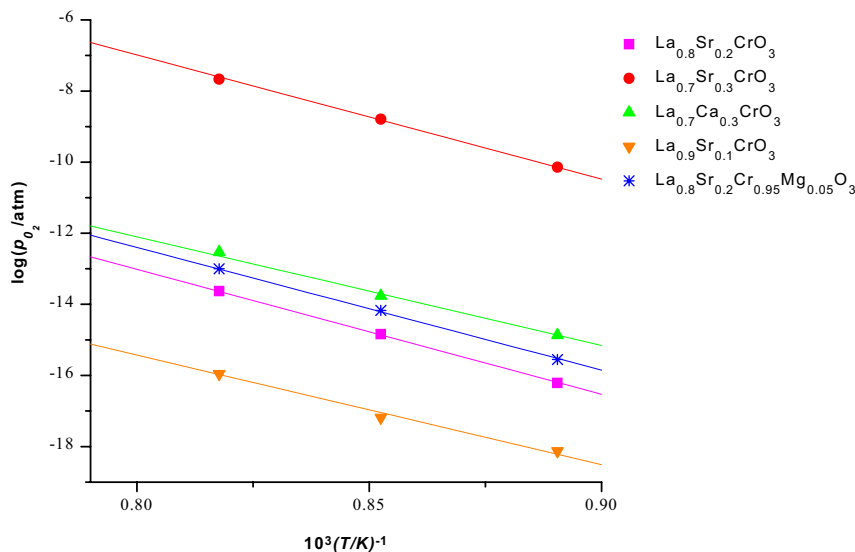


Fig. 4: The plot of  $\log p_{O_2}$  vs.  $1/T$  for the substituted lanthanum chromites.

## Conclusions

In the temperature range of 1073 - 1273 K, the partial molar free energy is a linear function of temperature for the studied compounds. The partial molar enthalpies and entropies are independent of temperature.

Both in the doped lanthanum manganites and lanthanum chromites the effect of Sr-doping is seen to be an increase of  $\Delta\bar{G}_{O_2}$  and  $\log p_{O_2}$  values, while the relative partial entropy is decreased to a more negative value. In the same temperature range, the partial molar enthalpy is strongly dependent upon cation size.

The observed dependence of the thermodynamic data on the Sr-content in the doped lanthanum chromite perovskites suggests that the oxygen vacancies can be easily formed when the Sr concentration is high.

The results obtained on the A- and B-site substituted compounds evidence the effect of the iron and magnesium content, inferring that substituents on the B-site causes not only the valence control effect, but also the strong interactions to the oxygen sublattice.

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