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CORRELATIONS BETWEEN THE NONSTOICHIOMETRY AND THE THERMODYNAMIC DATA OF PEROVSKITE-TYPE COMPOUNDS IN THE La-Sr-Mn-O SYSTEM[*]

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A solid state electrochemical technique has been employed in order to study the correlations between the thermodynamic properties and the compositional variables of some ABO_3 where A = La, Sr; B = Mn (Fe, Co) perovskite-type compounds. 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 in the temperature range of 1073 - 1273 K. The effect of the relative oxygen stoichiometry change on the thermodynamic properties is compared with the influence of the A- and B- sites dopants, as well as with the effect of the A-site stoichiometry change.

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1. Introduction

Among the conducting transition metal oxides with perovskite structure, the compounds in the system La-Sr-Mn-O 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.

The thermodynamic properties of the lanthanum strontium manganites are strongly affected not only by the strontium content, but also by the oxygen nonstoichiometry, as well as by the partial substitution of Mn on the B-site. Although the knowledge of the defect stucture has increased during the years, the relationships between the nonstoichiometric behaviour and thermochemical stability of many compounds has not been elucidated yet. The aim of this paper was to evidence the extent of the nonstoichiometry and the influence of different compositional variables on the thermodynamic properties.

The solid - oxide electrolyte galvanic cells method has been employed in order to characterize from the thermodynamic point of view some perovskite-type materials of general formula $(La_{1-x}Sr_x)_zMn_{1-y}Fe(Co)_yO_3$. 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 were determined as a function of temperature and composition within the range 1073-1273 K. The influence of the oxygen stoichiometry change on the thermodynamic properties was examined using the data obtained by a coulometric titration technique coupled with EMF measurements. The effect of different compositional variables on the thermodynamic properties is discussed being related with the variation of the predominant defects in the oxygen sublattice.

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2. Experimental

The experimental method and apparatus were previously described [1]. Their principal characteristics are as follows:

- The geometry of the work cell ensures a compact electrode - electrolyte assembly, so that temperature uniformity is easily reached.

- The measurements are performed in vacuum at a residual gas pressure of 10^{-5} - 10^{-6} Pa, after a previous rinsing of the equipment with purified argon.

- Prevention of signal pick-up from external heating sources is achieved by the use of a non-inductive furnace and by the adequate shielding of cell and leads.

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

(-) Sample (ABO_3) / $ZrO_2(Y_2O_3)$ / Fe, wüstite (+) (I)

- 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 powder of the specimens were 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 [2,3]. 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 compositions of the samples are listed in Table 1.

- The reference and also, the counter electrode in the case of coulometric titration measurements are both prepared from electrolytic iron (Koch-Light iron) and Fe_2O_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 h. Thus, small cylindrical samples of 2 mm diameter and 2 mm thickness were prepared.

Table 1. Composition of the specimens.

L1	$LaMnO_3$	S1	$(La_{0.70}Sr_{0.30})_{0.95}Mn_{0.80}Fe_{0.20}O_3$
L2	$La_{0.70}Sr_{0.30}MnO_3$	S2	$(La_{0.75}Sr_{0.25})_{0.95}Mn_{0.80}Fe_{0.20}O_3$
		S3	$La_{0.70}Sr_{0.30}Mn_{0.80}Fe_{0.20}O_3$
M1	$(La_{0.70}Sr_{0.30})_{0.95}MnO_3$	S4	$(La_{0.70}Sr_{0.30})_{0.95}Mn_{0.30}Fe_{0.70}O_3$
M2	$(La_{0.75}Sr_{0.25})_{0.95}MnO_3$	S5	$La_{0.75}Sr_{0.30}Mn_{0.30}Fe_{0.70}O_3$
		S6	$La_{0.70}Sr_{0.30}Mn_{0.50}Fe_{0.50}O_3$
		S7	$La_{0.70}Sr_{0.30}Mn_{0.45}Co_{0.05}Fe_{0.50}O_3$

The electromotive force was measured with a Keithley 197 microvoltmeter at 50 K intervals between 1073 and 1273 K, every time waiting until the equilibrium values are attained. By solid state coulometric titration [4] the precise change of the oxygen stoichiometry was obtained). The titration was performed at 1173 K. After the titration and equilibration, by changing the temperature under the open-circuit condition, the change of EMF with temperature was again determined.

3. Results and discussion

The free energy change of the cell is given by the classical expression:

$$\Delta G_{\text{cell}} = \mu_{O_2} - \mu_{O_{2(\text{ref})}} = 4FE \qquad (1)$$

where E is the steady state EMF of the cell in volts; μ_{O_2}, $\mu_{O_{2(\text{ref})}}$ are respectively, the oxygen chemical potentials of the perovskite and the reference electrode and F is the Faraday constant (F = 96.508 kJ/V equiv.). Upon substituting the experimental values of E in eq. (1) and knowing the free energy change of the reference electrode [5], the values of the relative partial molar free energy of oxygen dissolution in the perovskite phase can be calculated. The relative partial molar enthalpies and entropies, as well as the pressures of oxygen in equilibrium with the solid were obtained according to the well known relationships [1,4].

The obtained results are listed in Tables 2, 3 and depicted in Fig. 1 - 6. Within the temperature range of 1073-1273 K the partial molar free energy is a linear function of temperature. The partial molar entropies and enthalpies do not depend on temperature.

By comparing the two sets of data obtained for the undoped and Sr-doped compounds, one can observe that the $\Delta\overline{G}_{O_2}$ and $\log p_{O_2}$ values increase for the lanthanum strontium manganite comparatively with the values obtained for the undoped compound (Fig. 1 and 2). This observation can be explained by the increase of the oxygen vacancies concentration when La^{3+} ions are replaced by Sr^{2+} ions.

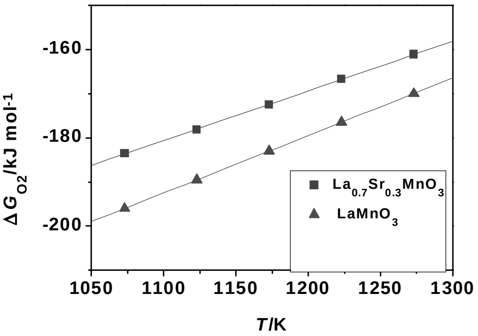

Fig. 1. The variation of $\Delta\overline{G}_{O_2}$ with temperature.

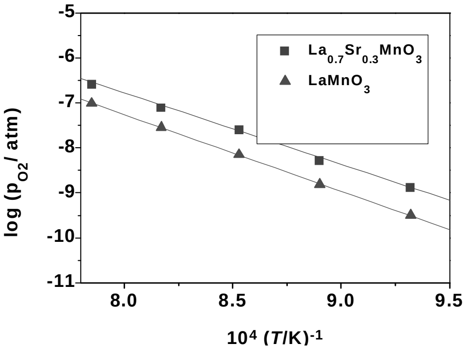

Fig. 2. The plot of $\log p_{O_2}$ versus 1/T.

The variation of the thermodynamic data vs stoichiometry have been evidenced by measurements on $LaMnO_{3-\delta}$ and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ with δ ranging from 0.019 to 0.053. As one can see from Table 2, in the case of Sr-doped compounds, the highest values are obtained for a small departure from stoichiometry. Between δ = 0.019 and δ = 0.046, both values of enthalpy and entropy decrease remarkably with δ, suggesting the change of the predominant defects. From δ = 0.046 to δ = 0.053, both $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ increase again.

Table 2. Relative partial molar thermodynamic data as a function of composition and oxygen nonstoichiometry (temperature range 1073-1273 K).

	$\Delta\overline{G}_{O_2} = \Delta\overline{H}_{O_2} - T\Delta\overline{S}_{O_2}$			
	$\Delta\overline{H}_{O_2}$ (kJ mol^{-1})		$\Delta\overline{S}_{O_2}$ (kJ mol^{-1} K^{-1})	
δ	$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	$LaMnO_{3-\delta}$	$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	$LaMnO_{3-\delta}$
0.019	-331.66 ± 7.7	-308.38 ± 6.0	-0.130 ± 0.01	-0.106 ± 0.01
0.046	-559.94 ± 7.9	-532.38 ± 7.8	-0.210 ± 0.01	-0.198± 0.01
0.053	-540.90± 8.0	-528.52 ± 7.9	-0.257 ± 0.01	-0.174 ± 0.01

Carrying out measurements by high temperature gravimetry, coulometric titration and iodometry on $La_{0.6}Sr_{0.4}MnO_{3-\delta}$, Mizusaki and coworkers [6] put also into evidence the decreasing of $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ for δ around 0.0225 and gradual increasing of the variations of the entropy with δ, for δ > 0.04. They come to the conclusion that the oxygen vacancies in the region of δ < 0.0225 would not be randomly distributed on all of the oxygen sites. Instead, for the region of $\delta > 0.04$, the oxygen vacancies distribute themselves randomly on the oxygen sublattice. This fact is confirmed by our data.

As one can see from the Table 3 and Fig. 3 - 6, the group of lanthanum strontium ferrite manganites is very well made distinct by the EMF values and by their thermodynamic data and the obtained results can be discussed only being related to the effect of the iron content. By the least squares analysis the relationships for the temperature dependences of E and $\Delta\overline{G}_{O_2}$ are found (Table 3) in which the standard deviations of the variables are considered. The $\Delta\overline{G}_{O_2}$ 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.

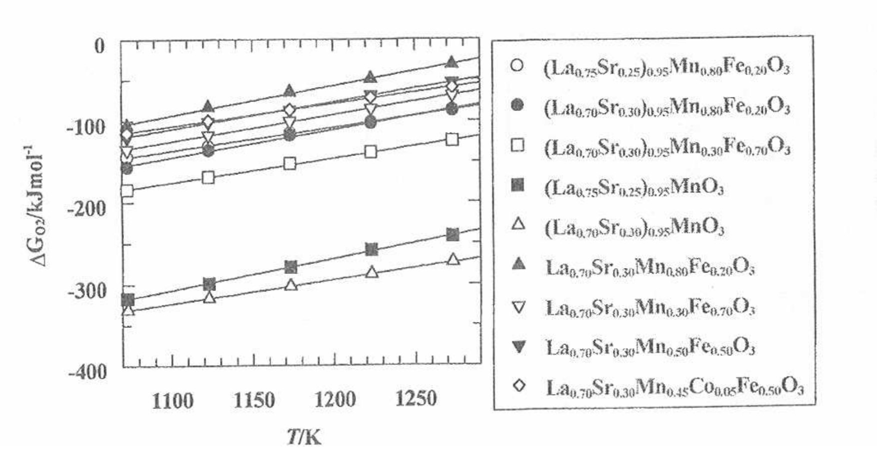

Fig. 3. The variation of $\Delta\overline{G}_{O_2}$ with the temperature for the selected compositions.

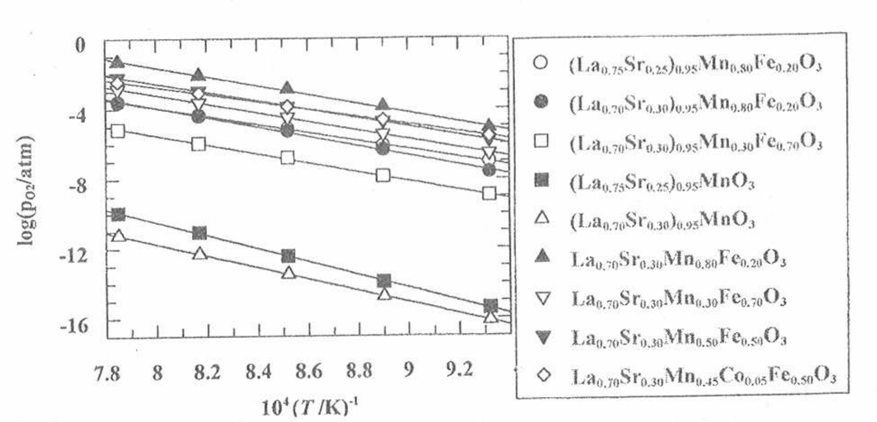

Fig. 4. The plot of log p vs. 1/T for the selected compositions.

As one can see in Fig. 5 and 6, a small variation in the strontium content of 5% gives a distinct change of partial molar quantities for the compounds without iron in comparison with the compounds in which iron is present. Thus, the increase in A-site substitution from x = 0.25 to x = 0.30 is followed by the increase of $\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ values with ~71 kJ mol^{-1} and ~81 J mol^{-1} K^{-1} respectively for the samples M1, M2 (in absence of iron) and by a decrease with ~57 kJ mol^{-1} and ~45 J·mol^{-1}·K^{-1} in the case of the samples S1, S2 (with 20% iron). The increase of these values in the first case can be an indication that the oxygen vacancies distribute randomly on the oxygen sublattice, while the decrease of

$\Delta\overline{H}_{O_2}$ and $\Delta\overline{S}_{O_2}$ values in the iron - containing samples suggest the increase of the binding energy of oxygen and an increase of order in the oxygen sublattice of the perovskite-type structure.

Table 3. EMF values of galvanic cells and calculated relative partial molar thermodynamic data for a solution of oxygen in LaSrMnO$_3$ phase (temperature range 1073-1273K).

Sample	E/V = A + BT		$\Delta\overline{G}_{O_2} = \Delta\overline{H}_{O_2} - T\Delta\overline{S}_{O_2}$	
	A	B	$\Delta\overline{H}_{O_2}$ (kJ·mol^{-1})	$\Delta\overline{S}_{O_2}$ (kJ·mol^{-1}·K^{-1})
S1 (before titration)	0.035 ± 0.002	5x10^{-4} ± 0	-521.92 ± 3.00	-0.343 ± 0.003
S1(after titration δ=0.04)	0.097 ± 0.003	5x10^{-4} ± 0	-498.16 ± 2.81	-0.312 ± 0.002
S2	0.181 ± 0.002	4x10^{-4} ± 0	-464.80 ± 2.09	-0.298 ± 0.002
S3	0.095 ± 0.002	6x10^{-4} ± 0	-498.78 ± 2.29	-0.369 ± 0.002
M1(before titration)	-0.288 ± 0.002	4x10^{-4} ± 0	-646.79± 2.57	-0.294 ± 0.002
M1(after titration δ=0.04)	-0.115± 0.002	2x10^{-4} ± 0	-579.91± 2.52	-0.226 ± 0.002
M2	-0.505± 0.002	6x10^{-4} ± 0	-718.63± 3.08	-0.375 ± 0.003

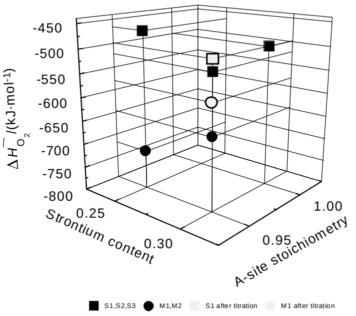

Fig. 5. $\Delta\overline{H}_{O_2}$ as a function of strontium content and A-site stoichiometry for the selected compositions listed in Table 1.

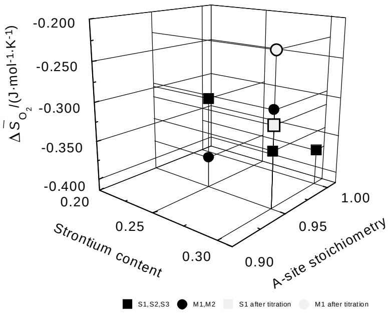

Fig. 6. $\Delta\overline{S}_{O_2}$ as a function of strontium content and A-site stoichiometry for the selected compositions listed in Table 2.

Referring to the $\Delta\overline{G}_{O_2}$ values (Fig. 3 and 4), the influence of such small variations in concentration of strontium ions is more evident in the group of lanthanum strontium manganites (samples M1 and M2) for which a difference of ~30 kJ mol^{-1} is obtained at 1273 K. In the case of the samples in which iron is present (samples S1, S2), variations of only ~10 kJ·mol^{-1} are found. At 50% iron, but at the same strontium content, the values of $\Delta\overline{G}_{O_2}$ and $\log p_{O_2}$ for the sample with 0.5% Co are very near to the values obtained for the sample without cobalt.

In Fig. 5,6 and Table 3, the effect of the oxygen stoichiometry change δ = 0.04 on the thermodynamic properties is compared with the influence of the strontium and iron dopants, as well as with the effect of the A-site stoichiometry change in the case of compounds in which iron is present. The $\Delta\overline{H}_{O_2}$ value (-498.16 kJ mol^{-1}) obtained after titration for the sample S1 with z = 0.95, is very close to the value of -498.78 kJ mol^{-1} obtained for the sample S3 with z = 1. This observation suggests that, due to the combined effect of Fe dopping on the B-site and the vacancies on the A-site, the amount of oxygen involved in the stoichiometry change of δ = 0.004 is very similar to that involved in the change of the A-site stoichiometry (Δz = 0.05). 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 [7,8] and is also confirmed by the observations of Teraoka in the study of the ionic conductivities and oxygen permeation in cobaltities doped by iron [9,10].

4. Conclusions

Within 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.

The effect of Sr-doping is seen to be an increase of $\Delta\overline{G}_{O_2}$ and $\log p_{O_2}$ values, while the relative partial entropy is decreased to a more negative value.

The group of lanthanum strontium ferrite manganites is very well made distinct by their thermodynamic data and the obtained results evidenced the effect of the iron content. The variation of thermodynamic properties with the oxygen stoichiometry change can be discussed only being related to the variation of the predominant defects in the oxygen sublattice.

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