Oxygen Nonstoichiometry of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (0 < x ≤ 0.6)

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The oxygen nonstoichiometry (δ) of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (0 < x ≤ 0.6) has been studied as a function of temperature (573–1673 K) and oxygen partial pressure (1–10^{-3} atm) using TGA and coulometric titration techniques. The absolute values of oxygen nonstoichiometry were determined by the direct reduction in a flux of hydrogen (TGA) or by decreasing P_{O_2} in a coulometric titration cell. The boundaries of phase stability of La$_{0.7}$Sr$_{0.3}$CoO$_{3-\delta}$ and (La$_{0.7}$Sr$_{0.3}$)$_2$CoO$_{4\pm\upsilon}$ were evaluated. A possible mechanism of disordering processes has been discussed. © 1990 Academic Press, Inc.

Introduction

Many of the useful properties such as catalytic activity (*1, 2*) and electron emission (*3, 4*) in the La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ complex oxides with the perovskite-type structure are a result of their electron structure and oxygen nonstoichiometry. External thermodynamic conditions [temperature (T) and partial oxygen pressure (P_{O_2})] during exploitation of such materials as catalysts (*2*) or electrodes (*4, 5*) vary widely. Thus knowledge of the effect of T and P_{O_2} disordering processes, in particular oxygen nonstoichiometry, is very important for the control of their properties.

In spite of the great interest in La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, until recently only the thermodynamic stability (*6, 7*) and oxygen nonstoichiometry (*8, 9*) of undoped LaCoO$_{3-\delta}$ (x = 0) had been investigated.

In the present study the oxygen nonstoichiometry of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ as a function of T and P_{O_2} is investigated.

Experimental

Lanthanum oxide (La$_2$O$_3$), cobalt hydroxide (Co(OH)$_2$), and strontium carbonate (SrCO$_3$), with purities of not less than 99.9%, were used as starting materials. All were subjected to a preliminary anneal in air during which Co(OH)$_2$ decomposed to Co$_3$O$_4$ at 800°C according to the reaction

$$3Co(OH)_2 + \tfrac{1}{2}O_2 = Co_3O_4 + 3H_2O. \quad (1)$$
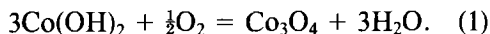
The La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (x = 0.1, 0.3, 0.6) samples were prepared by the usual ceramic technique of three-step firing in the temperature range 850–1050°C in air for 20–25 hr:

$$3(1 - x)\,La_2O_3 + 2Co_3O_4$$
$$+ 6x\,SrCO_3 + (1 + 3x - 6\delta)/2\,O_2$$
$$= 6La_{1-x}Sr_xCoO_{3-\delta} + 6x\,CO_2. \quad (2)$$
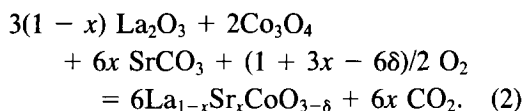
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All samples were identified by X-ray powder diffraction using Co$K\alpha$ radiation to be single phase with a perovskite-type structure.

The changes of oxygen nonstoichiometry were determined using a TGA technique (9) and $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ was also examined by coulometric titration in a solid electrolyte $(0.9ZrO_2 + 0.1Y_2O_3)$ cell.

The TGA measurements were made in the temperature range 573–1673 K and at oxygen partial pressures of 10^{-3}–1 atm. The range of temperatures and pressures investigated varied with sample composition depending on the decomposition pressures and temperatures of the specimen. Different oxygen pressures were obtained by mixing helium and air in appropriate ratios and controlled using an oxygen sensor (ZrO_2 doped by Y_2O_3), which was located just under the sample in the TGA cell. The accuracy of control of the thermodynamic parameters was $\Delta\log(P_{O_2}/atm) = \pm0.05$, $\Delta T = \pm0.5$ K; the maximum error in the measuring of weight changes was $\pm2 \cdot 10^{-3}\%$.

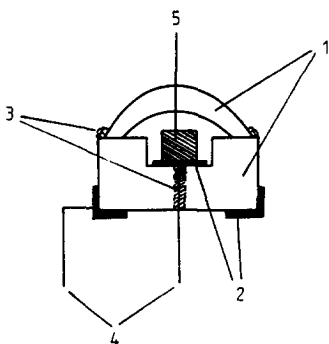The coulometric cell made from $0.9ZrO_2 + 0.1Y_2O_3$ ceramic is shown in Fig. 1. The cell, with the sample inside, was sealed with special glue fused at $T > 1500$ K. The internal free volume of the cell was about $8.65 \cdot 10^{-2}$ cm^3. The cell was placed into the device described earlier (6, 7), which provided control of the partial oxygen pressure ($1 < P_{O_2} < 10^{-14}$) on the reference electrode of the cell with the help of an oxygen pump and sensor over the temperature range 1000–1473 K. The accuracy of control of the thermodynamic parameters of the cell was $\Delta\log P_{O_2} = \pm0.02$, $\Delta T = \pm0.5$ K.

Special attention was given to the establishment of equilibria. Thermodynamic equilibrium states were confirmed by observing constant mass in TGA experiments and constant emf in coulometric titration measurements while approaching the same conditions of T and P_{O_2} from different sides (i.e., while changing T in isobaric experiments, or varying P_{O_2} in isothermal studies). The period required to establish equilibrium between the gaseous state and sample varied from 10–15 min to 3–4 hr depending on the temperature and oxygen pressure ranges involved.

Figure 2 illustrates some isobaric dependencies of relative mass changes ($\Delta m/m_0$) versus temperature in TGA experiments. The reversibility of mass changes proved that there were no other exchanges between solid and gaseous phases except involving oxygen,

$$La_{1-x}Sr_xCoO_{3-\delta_0} = La_{1-x}Sr_xCoO_{3-\delta}$$
$$+ (\Delta\delta/2)O_2 \quad (3)$$
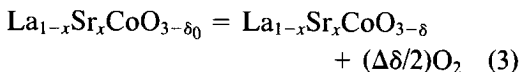
$$\Delta\delta = \delta - \delta_0 = (\Delta m/m_0) \cdot M/M_0, \quad (4)$$

where m_0 is the mass of the sample under the initial conditions of experiment T_0, $P_{O_2 0}$; δ_0 is the oxygen nonstoichiometry at initial conditions; $\Delta\delta$ and δ are the relative and absolute values of oxygen nonstoichiometry at all other T and P_{O_2}; M is the molar mass of complex oxide $La_{1-x}Sr_x CoO_{3-\delta}$; and M_0 is the atomic mass of oxygen.

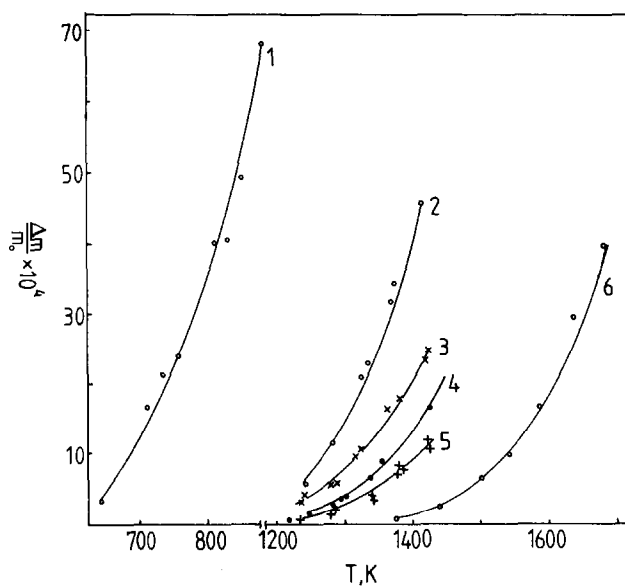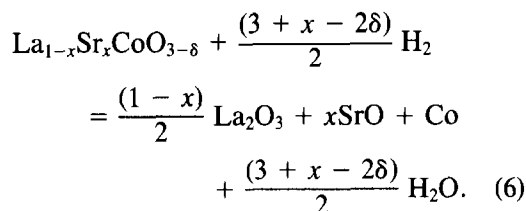The calculations of relative oxygen nonstoichiometry in the coulometric titration

FIG. 1. The construction of the coulometric titration cell. 1, solid electrolytes $(0.9ZrO_2 + 0.1Y_2O_3)$; 2, porous Pt electrodes; 3, special glue; 4, Pt wires; 5, sample.

FIG. 2. The relative mass changes of the $La_{0.9}Sr_{0.1}CoO_{3-\delta}$ (1); $La_{0.4}Sr_{0.6}CoO_{3-\delta}$ (2–5) and $LaCoO_{3-\delta}$ (6) (9) as a function of temperature at different oxygen pressures: 1, 4, 6, at $\log P_{O_2} = -0.68$; 2, at $\log P_{O_2} = -2.2$; 3, at $\log P_{O_2} = -1.1$; 5, at $\log P_{O_2} = 0$.

method can be performed using the following equation,

$$\Delta\delta = (2M/m_0)[Q/4F - (V/RT)(P_{O_2} - P'_{O_2})],$$ (5)

where Q is the amount of electric charge passed through the cell, V is the free volume of the cell, and P_{O_2} and P'_{O_2} are the equilibrium oxygen partial pressures before and after each passage of titration current through the cell.

The absolute values of oxygen nonstoichiometry of the complex oxides at 973 K and $P_{O_2} = 0.21$ atm were determined by full reduction in thermobalances according to the reaction

$$La_{1-x}Sr_xCoO_{3-\delta} + \frac{(3 + x - 2\delta)}{2} H_2$$

$$= \frac{(1 - x)}{2} La_2O_3 + xSrO + Co$$

$$+ \frac{(3 + x - 2\delta)}{2} H_2O.$$ (6)

It is assumed that the oxygen nonstoichiometry values of the simple lanthanum and strontium oxides are negligible compared with the complex oxides. Each composition (x) was reduced not less than three times. Results obtained were reproducible within the accuracy of the method (Table I).

The full decomposition of the sample in the coulometric titration method was carried out inside the cell by the electrochemi-

TABLE I

AVERAGE VALUES OF OXYGEN NONSTOICHIOMETRY IN $La_{1-x}Sr_xCo$ $O_{3-\delta}$ AT 973 K IN AIR FROM HYDROGEN REDUCTION EXPERIMENTS

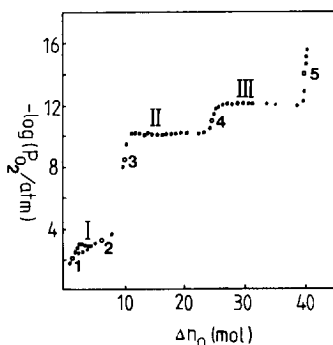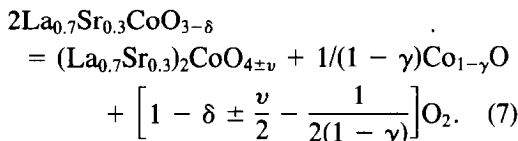| x	δ
0.1	0.0153
0.3	0.0213
0.6	0.175

FIG. 3. The titration curve for the $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ at 1383 K.

cal removal of oxygen. The reduction curve for 1373 K is shown in Fig. 3. In separate experiments to identify the phases involved, $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ samples were annealed at different oxygen pressures with subsequent XRD examination, which are marked on Fig. 3 by points. It was proved that in the pressure range in the vicinity of point 1 (Fig. 3) the oxygen exchange process corresponds to reaction 3. Further decreasing the oxygen pressure leads to the decomposition of the complex oxide according to the reaction

$$2La_{0.7}Sr_{0.3}CoO_{3-\delta}$$
$$= (La_{0.7}Sr_{0.3})_2CoO_{4\pm\nu} + 1/(1 - \gamma)Co_{1-\gamma}O$$
$$+ \left[1 - \delta \pm \frac{\nu}{2} - \frac{1}{2(1 - \gamma)}\right]O_2. \quad (7)$$

Plateau I on the titration curve (Fig. 3) corresponds to equilibrium of reaction 7. The second plateau II corresponds to the decomposition of cobalt oxide:

$$Co_{1-\gamma}O = (1 - \gamma)Co + \tfrac{1}{2}O_2. \quad (8)$$
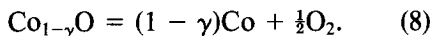
The last plateau, III, corresponds to the decomposition of the complex oxide $(La_{0.7}Sr_{0.3})_2CoO_{4\pm\nu}$ formed during reaction 7:

$$(La_{0.7}Sr_{0.3})_2CoO_{4\pm\nu} = 0.7La_2O_3$$
$$+ 0.6SrO + Co + (1.3 \pm \nu)/2O_2. \quad (9)$$
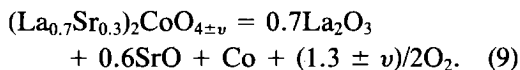
Using the observed values of the equilibrium partial pressures of oxygen for the re-

actions 7 and 9 at 1383 K,

plateau I $\log(P_{O_2}/\text{atm}) = -2.8$ and

plateau III $\log(P_{O_2}/\text{atm}) = -12.0$,

the standard Gibbs potentials of these reactions were obtained (the values of oxygen nonstoichiometry of oxides involved in the reactions were not taken into account).

Reaction 7: $\Delta G_0(1383 \text{ K})$
$$= -RT/2 \ln P_{O_2} = 37 \text{ (kJ/mol)}. \quad (10)$$

Reaction 9: $\Delta G_0(1383 \text{ K})$
$$= -1.3RT/2 \ln P_{O_2} = 206 \text{ (kJ/mol)}. \quad (11)$$

The absolute value of oxygen nonstoichiometry of $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ was calculate from point 5 on the titration curve. The isothermal dependencies of oxygen nonstoichiometry versus oxygen partial pressure obtained from the coulometric titration measurements are shown in Fig. 4.

Discussion

From the results of TGA and coulometric titration measurements and the absolute values of nonstoichiometry, the isobaric and isothermal dependencies of oxygen nonstoichiometry of the complex oxides have been obtained. They were computed

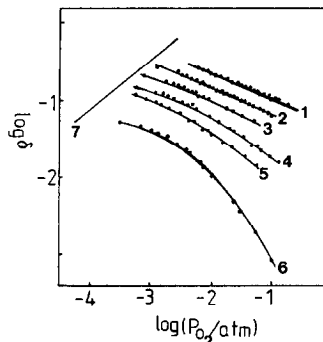
FIG. 4. Isothermal dependencies of oxygen nonstoichiometry (1–6) and the boundary of stability (7) for the $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ from coulometric titration measurements: 1, 1433 K; 2, 1383 K; 3, 1342 K; 4, 1293 K; 5, 1253 K; 6, 1193 K.

TABLE II

COEFFICIENTS OF ISOBARIC DEPENDENCES OF OXYGEN NONSTOICHIOMETRY OF
$La_{1-x}Sr_xCoO_{3-\delta}$ $\log \delta = A + BT^{-1} + CT^{-2}$

x	$\log(P_{O_2}/\text{atm})$	A	B	$C * 10^{-6}$	Temperature interval	$\pm\Delta\log \delta$
0.1	0	8.8330	−25055	14.845	1233–1426	0.01
	−0.68	4.9110	−13913	7.119	1113–1607	0.01
	−1.1	4.6492	−12435	5.7661	1237–1421	0.007
	−1.4	5.4219	−14592	7.5099	1273–1423	0.02
	−2.2	4.4666	−11259	5.0153	1323–1425	0.006
0.3	0	−1.7847	4483.8	−4.816	1173–1473	0.003
	−0.68	2.2230	−5853.2	2.011	839–1676	0.02
	−1.13	1.1089	−3261.9	0.689	1173–1423	0.002
	−1.6	1.0769	−3074.3	0.582	1163–1423	0.008
0.3 Coulometric titration	0	−32.59	92170	−67.4	1100–1433	0.08
	−0.5	−23.45	66367	−49.13	1100–1433	0.05
	−1.0	−15.86	45021	−34.04	1100–1433	0.03
	−1.5	−9.64	27640	−21.69	1100–1433	0.01
	−1.75	−6.99	20331	−16.52	1100–1433	0.01
	−2.00	−4.79	14252	−12.3	1100–1433	0.008
	−2.5	−1.11	4308	−5.22	1100–1433	0.01
	−2.75	−0.269	2061	−3.91	1100–1433	0.01
0.6	0	0.3756	−1470.3	0.3029	514–1424	0.004
	−0.68	0.3746	−1407.5	0.297	558–1660	0.002
	−1.24	0.2215	−1061.1	0.145	648–1386	0.002
	−1.51	0.2217	−1036.2	0.135	660–1422	0.002

by statistical methods and the coefficients of the resulting equations are listed in Tables II and III.

The oxygen nonstoichiometries of $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ obtained from TGA are slightly higher than those given by the coulometric titration, but these differences diminish with increasing T and decreasing P_{O_2} (Table IV). The possible reason for these differences may be connected with the different samples used in the two methods, i.e., powder samples in TGA and sintered pellets in coulometric titration. This means that the surface areas of the samples are different and thus the contribution of the absorption processes which can take place on the surfaces (10) are different.

It is easy to see that the value of oxygen nonstoichiometry in $La_{1-x}Sr_xCoO_{3-\delta}$ essentially increases with increasing strontium content (Fig. 5). The substitution of Sr^{2+} ions for La^{3+} leads to the partial oxidation of proportional amounts of Co^{3+} ions to Co^{4+} (or in quasichemical notation $Co^{\cdot}_{Co}$). However, this oxidation state of cobalt ions is unstable and charge neutralization partially occurs by means of oxygen vacancies:

$$2Co^{\cdot}_{Co} + O^x_O = V^{\cdot\cdot}_O + 2Co^x_{Co} + \tfrac{1}{2}O_2. \quad (12)$$
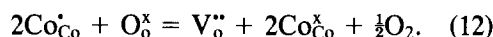
Thus, the chemical formula of the complex oxide can be written as follows:

$$La_{1-x}Sr_xCo^{+3}_{1-x+2\delta}Co^{+4}_{x-2\delta}O_{3-\delta}. \quad (13)$$

Assuming this model many investigators have determined the oxygen nonstoi-

TABLE III

Coefficients of Isothermal Dependencies of Oxygen Nonstoichiometry of
$La_{1-x}Sr_xCoO_{3-\delta}$ $\log \delta = A' + B'\log(P_{O_2}) + C'(\log(P_{O_2}))^2$

x	$T(K)$	A'	B'	C'	Pressure interval	$\pm\Delta\log\delta$
0.1	1273	−1.718	−0.1876	0	1–6.3 $*$ 10^{-3}	0.03
	1373	−1.559	−0.2127	0		0.03
	1423	−1.462	−0.2162	0		0.03
0.3	1173	−1.442	−0.2124	0	1–2.5 $*$ 10^{-2}	0.03
TGA	1273	−1.2458	−0.1744	0		0.02
	1373	−1.074	−0.1436	0		0.01
	1473	−0.9955	−0.1300	0		0.01
0.3	1193	−2.874	−0.974	−0.138	1–1.78 $*$ 10^{-3}	0.01
Coulometric	1253	−1.949	−0.446	−0.042		0.01
titration	1293	−1.851	−0.499	−0.066		0.01
	1342	−1.460	−0.273	−0.020		0.01
	1383	−1.328	−0.225	−0.009		0.01
	1433	−1.162	−0.172	−0.001		0.01
0.6	673	−1.1276	−0.0704	0	1–3.1 $*$ 10^{-2}	0.02
	873	−0.9091	−0.0783	0		0.01
	1173	−0.6585	−0.0635	0		0.005
	1273	−0.5932	−0.0572	0		0.005
	1373	−0.5351	−0.0509	0		0.005
	1423	−0.5084	−0.0478	0		0.006

chiometry by means of iodometric titration
(*11*). However, the model does not take
into account at least two possible factors
which may influence the value of oxygen

TABLE IV

Comparison of Oxygen Nonstoichiometry in
$La_{1-x}Sr_xCoO_{3-\delta}$ Obtained from TGA and Coulo-
metric Titration Experiments

$\log(P_{O_2}/atm)$	$T(K)$	$\log \delta^a$	$\log \delta^b$
−0.68	1253	−1.16	−1.66
	1383	−0.96	−1.18
	1433	−0.88	−1.04
−1.6	1253	−1.00	−1.34
	1383	−0.84	−0.99
	1433	−0.78	−0.89

[a] Obtained from TGA measurements.
[b] Obtained from coulometric titration results.
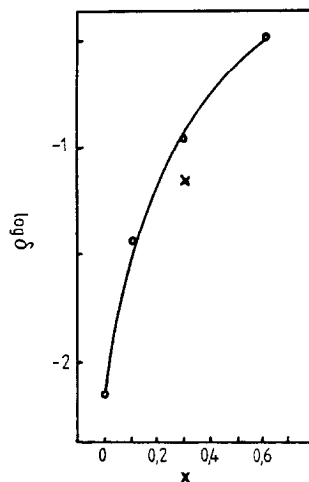

Fig. 5. The oxygen nonstoichiometry for the La_{1-x}
$Sr_xCoO_{3-\delta}$ as a function of strontium content (x) at
1373 K in air.

TABLE V

VALUES OF MOLAR ENTHALPY OF OXYGEN VACANCY FORMATION ΔH (kJ/mol) IN THE
La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ FROM TGA EXPERIMENTS

x	δ log P_{O_2}	0.04	0.06	0.08	0.1	0.12	0.14	0.16	0.2	0.3
0.1	0	85.6	105.6							
	−0.68	71.3	83.0	90.6	96.1					
	−1.11	74.5	83.7	89.8	94.2					
	−1.40	54.1	69.9	79.1	85.3					
	−2.30	57.6	68.0	74.5	79.1					
0.3	0	68.7	57.2	49.8	43.6	38.6				
	−0.68	43.2	48.9	52.5	55.1	57.3				
	−1.13	37.3	39.2	40.5	41.6	42.3				
	−1.60	36.3	38.6	40.2	41.4	42.3				
0.6	0			20.3	21.1	21.7	22.2	22.5	23.2	24.1
	−0.68			9.15	11.25	12.67	13.77	14.58	16.04	18.26
	−1.24			11.51	12.37	13.04	13.56	14.01	14.73	15.99
	−1.51			11.45	12.27	12.89	13.39	13.82	14.50	15.65
	−1.77			12.1	12.86	13.45	13.93	14.34	14.58	16.10

nonstoichiometry: (i) The ratio of cobalt ions in the different valence states at high temperatures is strongly influenced by intrinsic electron disordering, which can take place in such systems (12):
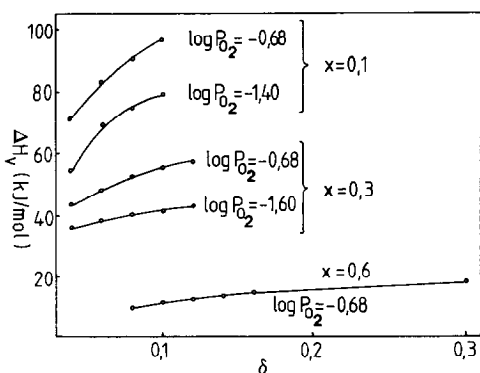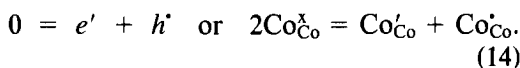
$$0 = e' + h^{\cdot} \quad \text{or} \quad 2Co_{Co}^x = Co_{Co}' + Co_{Co}^{\cdot}. \tag{14}$$

FIG. 6. The molar enthalpy of disordering processes (ΔH_v) for La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ as a function of oxygen nonstoichiometry.

(ii) Oxygen nonstoichiometry can be realized not only through the existence of $V_o^{\cdot\cdot}$, but as a sum of differently charged vacancies:

$$\delta = [V_o^{\cdot\cdot}] + [V_o^{\cdot}] + [V_o^x]. \tag{15}$$

Thus, we consider that the method of hydrogen reduction or reduction by decreasing of oxygen pressure gives more accurate results in the determination of oxygen nonstoichiometry.

It is not possible to calculate the concentration of oxygen vacancies, because of the second reason mentioned above and the inclination of these structures to form superstructures by means of crystallographic displacement. Nevertheless an enthalpy of the disordering processes may be evaluated, using the equation below,

$$\delta = q \cdot P_{O_2}^{1/m} \cdot \exp(\Delta S_v/R) \cdot \exp(-\Delta H_v/RT). \tag{16}$$

where q is a correlation coefficient, appropriate to the point defect model, and ΔS_v

and ΔH_v are the effective entropy and enthalpy of disordering processes, respectively.

At constant P_{O_2}:

$$\Delta H_v = -R[\partial \ln \delta / \partial (1/T)]. \qquad (17)$$

It will be seen that the enthalpy of disordering processes (Table V) decreases with increasing strontium content. The nonlinear dependence of ΔH_v versus δ (Fig. 6) indicates a complicated character for the disordering processes, which could not be described by the point defects model.

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