THE SrO-Cr₂O₃-La₂O₃ PHASE DIAGRAM AND VOLATILITY OF Laₙ₋ₓSrₓCrO₃
(x = 0 - 0.3) IN COMPARISON TO Cr BASE INTERCONNECT ALLOYS

D.H. Peck, M. Miller*, H. Nickel, D. Das**, and K. Hilpert

Institute for Materials in Energy Systems, Research Centre Jülich, P.O. Box 1913,
52425 Jülich, Germany
* on leave from Technical University of Wroclaw, 50370 Wroclaw, Poland
** on leave from Bhabha Atomic Research Centre, Bombay, India

ABSTRACT
The thermodynamic properties and volatility of SOFC materials is an important aspect in order to guarantee the necessary long term operation of an SOFC. Contributions to the SrO-Cr₂O₃-La₂O₃ phase diagram were experimentally determined for the reducing and oxidizing conditions present in SOFCs. Moreover, the vaporization of Laₙ₋ₓSrₓCrO₃ was elucidated by the use of Knudsen effusion mass spectrometry. The results obtained were used in the evaluation of the thermochemical properties of this phase and of its volatility. The latter is compared with that of Cr base interconnect alloys. Degradation mechanisms due to Cr vaporization are discussed. Moreover, the results are employed for the prediction of the SrCO₃ formation in Laₙ₋ₓSrₓCrO₃ in the presence of CO₂ containing fuel gas.

1. INTRODUCTION
The materials generally used as interconnect (1-3) in solid oxide fuel cells (SOFC) are acceptor doped LaCrO₃ and chromium base alloys. MgO is used as dopant in the Westinghouse tubular concept (4), CaO makes possible liquid phase sintering (see e.g. Ref. 5) and SrO doping is preferred by Domier (6). The oxide dispersion strengthened alloy Cr5Fe1Y2O₅ is for example employed as metallic interconnect (7, 8, 9).

Knowledge on high temperature chemistry and thermodynamics of the interconnect materials under the oxidizing and reducing conditions at the electrodes is necessary in order to guarantee long term operation of an SOFC. The vaporization processes in the different atmospheres at the anode and cathode sides have to be known under operating conditions. Vaporization is also important for the sintering carried out at temperatures up to 1900 K in order to obtain high density. It has been shown that vaporization under operating conditions can lead to a rapid degradation of the electrical properties of an SOFC with a metallic interconnect due to chromium vaporization (7,8). Knowledge on
the potential for the decrease of this vaporization by the use of a LaCrO₃ base ceramic interconnect is, therefore, necessary. A further problem might be the alkaline earth carbonate formation at LaCrO₃ base interconnects if H₂/CO₂ anode gases are used (10). Thermodynamic activities of the alkaline earth metal in the LaCrO₃ base perovskites have to be known in order to make possible precise predictions on the carbonate formation.

In spite of the mentioned problems knowledge on the thermochemistry and vaporization of the LaCrO₃ base materials is very scanty. Yokokawa et al. (11) estimated the thermochemical properties of LaCrO₃ and phase equilibria in the La-M-Cr-O system (M=Mg,Ca,Sr). These authors rejected the experimental values on the Gibbs energy of formation of LaCrO₃ from the oxides La₂O₃ and Cr₂O₃ obtained by EMF measurements as ΔG°\text{1273 K} = -30.1±1.5 kJ mol⁻¹ (12) and ΔG°\text{1000 K} = -21.2±0.4 kJ mol⁻¹ (13). These values as well as the estimated value (11) deviate substantially from each other. The vaporization of LaCrO₃ base perovskites has essentially been investigated by the weight change (14) and by employing the transpiration method (15). The identification of the vaporizing species, which is a necessary prerequisite for the complete elucidation of the vaporization process, has not been carried out so far.

In this work systematic experimental investigations on the SrO-Cr₂O₃-La₂O₃ system and the Sr doped LaCrO₃ perovskite are reported for the first time. The following studies were carried out in order to clarify the items raised:
- contribution to the SrO-Cr₂O₃-La₂O₃ phase diagram under low O₂ partial pressure,
- vaporization studies of the perovskites LaₓSrₓCrO₃ (x = 0 - 0.3),
- computation of the chromium volatility of LaₓSrₓCrO₃ on the basis of the experimental data determined and comparison with the volatility of chromium base alloys,
- thermodynamic computations concerning the formation of SrCO₃ in interconnect materials.

2. EXPERIMENTAL

Perovskites of the compositions LaₓSrₓCrO₃ (x = 0, 0.10, 0.15, 0.20, 0.25, 0.30) and further samples of the compositions shown in Table 1 and Figure 1 were prepared by melting and decomposition of the respective nitrates. La(NO₃)₃·6H₂O, Sr(NO₃)₂, and Cr(NO₃)₃·9 H₂O (each analytic grade) supplied by Merck, Darmstadt, Germany, were used as starting materials. The samples were calcined at temperatures between 1473 and 1673 K for 10 h. The phase compositions of the samples was determined by XRD studies. The samples LaₓSrₓCrO₃, x = 0 - 0.3, consisted only of one phase.

The phase diagram studies were conducted by annealing the samples at 1873 K over 16 to 20 h and subsequent quenching on a water cooled Cu plate. This was carried out under air and in vacuum at low O₂ partial pressures (about 10⁻⁹ bar) which are also present during the vaporization studies of the same samples in the Knudsen cell. The
quenched samples were characterized by XRD studies and electron probe micro analysis of polished sections.

The vaporization studies were carried out by Knudsen effusion mass spectrometry (see e.g. Refs. 16, 17). The instrument of the type MAT 271 was supplied by Finnigan MAT, Bremen, Germany, and is completely controlled by a computer. The vapour species were ionized with an emission current of 1 mA and an electron energy of 50 eV. A Knudsen cell made of tungsten and lined completely with iridium was employed in the measurements. The diameter of the knife-edged effusion orifices amounted to 0.3 and 0.5 mm. Temperatures were measured with an automatic pyrometer of the type ETSO-U supplied by Dr. Georg Maurer GmbH, Kohlberg, Germany, and calibrated using the melting points of silver, gold, and platinum.

3. RESULTS

3.1 Phase Diagram Studies

The results of the phase diagram studies for low oxygen pressures carried out under vacuum are shown in Figure 1. The isothermal section shows the presence of 3 ternary oxide phases, in addition to the La_{1-x}Sr_xCrO_3 perovskite. These phases were identified as the Ruddlesden-Popper (18) phases (La,Sr)_2CrO_4, (La,Sr)_3Cr_2O_7, and (La,Sr)_4Cr_3O_10. The X-ray diffraction patterns of the relevant samples in general showed the lines of all three or at least of two Ruddlesden-Popper phases. All Ruddlesden-Popper phases were only present at low oxygen pressures, they disappeared completely after annealing the samples in air. Figure 2 shows the X-ray powder diffraction patterns of the sample of the composition (La_{0.5}Sr_{0.5})_2CrO_4. The patterns were obtained by annealing and quenching the same sample in vacuum and subsequently in air. It was shown that the formation and disappearing of the Ruddlesden-Popper phases was reversible. A detailed description of the phase diagram studies will be given elsewhere (19).

3.2 Thermochemical Properties of La_{1-x}Sr_xCrO_3

Upon vaporizing the different samples of the SrO-Cr_2O_3-La_2O_3 system with the Knudsen cell - mass spectrometer system the gaseous species Cr, CrO, CrO_2, Sr, SrO and LaO were identified and their partial pressures determined. Pure Cr_2O_3(s) was used for the pressure calibration. Details on the pressure determination will be given elsewhere (20), general aspects are reported in Refs. 16, 17.

The pressure determination in this work was carried out for the Cr_2O_3-poor boundary of the La_{1-x}Sr_xCrO_3 homogeneity range with sample compositions in the two- and three-phase fields (cf. Fig. 1). Such compositions were reached since the partial pressures of the Cr containing species are the highest, thereby leading to a Cr_2O_3 depletion in the condensed phase due to the effusion through the orifice in the Knudsen cell. It has to be expected that data for the Cr_2O_3-poor boundary of the La_{1-x}Sr_xCrO_3 homogeneity range are also relevant for practical application due to vaporization losses.
during the sintering. The results obtained for the $\text{Cr}_2\text{O}_3$ depleted samples agreed well with those which contain after their preparation the perovskite phase of similar chemical composition as the $\text{Cr}_2\text{O}_3$ depleted samples. The initial compositions of the latter samples belong to the Cr$_2$O$_3$-poor phase fields adjacent to La$_{1-x}$Sr$_x$CrO$_3$ (cf. Fig. 1).

Table 1 contains information on the measurements carried out and gives at 2000 K the measured partial pressures of the different species observed with the exception of $\text{O}_2$. The $\text{O}_2$ partial pressure was computed from the equilibrium constant of the reaction, $\text{Cr}(g) + 1/2 \text{O}_2(g) = \text{CrO}(g)$, by using the measured $\text{Cr}(g)$ and $\text{CrO}(g)$ partial pressures as well as the values of the equilibrium constant of this reaction from the literature (21). The values of the $\text{O}_2$ partial pressures obtained are given in Table 1. Figure 3 shows as an example the results of vapour pressure measurements over a Cr$_2$O$_3$-rich and Cr$_2$O$_3$-poor perovskite.

Thermodynamic activities of $\text{Cr}_2\text{O}_3$ in the samples were determined by considering the equilibria of $\text{CrO}(g)$ and $\text{CrO}_2(g)$ (method 1) as well as of $\text{Cr}(g)$ and $\text{CrO}(g)$ (method 2) with pure $\text{Cr}_2\text{O}_3(s)$ (calibration measurement) and the $\text{Cr}_2\text{O}_3$ in La$_{1-x}$Sr$_x$CrO$_3$ (measurement of samples). The procedure is reported in Ref. 20. The averages of the activities obtained by the two methods were taken as selected values. The deviation of the two values from the average was less than 7%. The mean values of the thermodynamic activities of $\text{Cr}_2\text{O}_3$ are shown in Fig. 4. In addition, the thermodynamic activities of SrO and La$_2$O$_3$ are given. Their determination and the evaluation of Gibbs energies of formation for La$_{1-x}$Sr$_x$CrO$_3$ will be published elsewhere (22). The determination of the thermodynamic activity of $\text{Cr}_2\text{O}_3$ in LaCrO$_3(s)$ which is in equilibrium with La$_2$O$_3(s)$, $a(\text{Cr}_2\text{O}_3) = 5.1 \times 10^{-3}$ (cf. Fig. 4) will be reported in Ref 20 in detail. The thermodynamic properties for the formation of LaCrO$_3$, $\Delta H_{298}^0 = -81.5 \pm 4.6$ kJ mol$^{-1}$ and $\Delta S_{298}^0 = 0.2 \pm 4.9$ J mol$^{-1}$ K$^{-1}$, according to the reaction

$$\frac{1}{2} \text{Cr}_2\text{O}_3(s) + \frac{1}{2} \text{La}_2\text{O}_3(s) = \text{LaCrO}_3(s)$$

are also reported in this paper.

4. DISCUSSION

4.1 Phase Diagram Studies and Thermodynamic Data

The difficulty in the preparation of single phase Ruddlesden-Popper phases can be explained by the similar thermodynamic stabilities (23) and the very similar crystal structure of these compounds. The difficulty was also observed by other workers for the Ruddlesden-Popper phases La$_{n+1}$Ni$_n$O$_{3n+1}$ (24). The results of this work (cf. Fig. 2) showed that the (La,Sr)$_2$CrO$_4$ phase predicted by Ref. 11 in the SrO-Cr$_2$O$_3$-La$_2$O$_3$ system in air is not present under these conditions. A survey on some Ruddlesden-Popper
phases observed and on their properties is given in Ref. 25 and the references quoted therein.

The thermodynamic properties for the formation of LaCrO$_3$ obtained in this work (Section 3.2) support the value $\Delta G^{298}$ = -70.7 kJ mol$^{-1}$ estimated by Yokokawa et al. (11), they differ substantially from the previous experimental values (Section 1).

4.2 Volatility of Chromium Under Operating Conditions at the Cathode Side

It is interesting to compare the chromium vaporization from a metallic interconnect with that of a LaCrO$_3$ based perovskite (cf. Section 1). Therefore, the volatility of chromium from La$_{1-x}$Sr$_x$CrO$_3$ ($x=0-0.3$) was computed for air used as oxidant at the cathode side of the fuel cell. The humidity of normal air at 25 °C amounts to 60% corresponding to $p$(H$_2$O)=0.02 bar. The H$_2$O partial pressure at the cathode side can be higher than 0.02 bar due to a possible leak in the electrolyte or interconnect. The formation of the chromium containing gaseous oxide (CrO$_3$, CrO$_2$, CrO), oxyhydroxide (CrO$_3$(OH)$_2$, CrO$_2$(OH)$_2$, CrO(OH)$_2$, CrO(OH)$_3$, CrOOH) and hydroxide species (CrOH, Cr(OH)$_2$, Cr(OH)$_3$, Cr(OH)$_4$, Cr(OH)$_5$, Cr(OH)$_6$) as well as gaseous Cr were taken into account. The computation was carried out by employing the thermodynamic activities of Cr$_2$O$_3$ given in Figure 4 as well as the thermodynamic data of the gaseous species given by Ebbinghaus (21). It was conservatively assumed that the thermodynamic activity of Cr$_2$O$_3$ does practically not decrease on going from 2000 K (Figure 4) to the SOFC operating temperature used in the computations (1223 K). The assumption is supported by the very small value for the entropy of formation of LaCrO$_3$ (Section 3.2). Figures 5 and 6 show the partial pressures obtained for the abundant gaseous species. The partial pressures computed by us (7) for a chromium base alloy are additionally given in Figure 6 for comparison. Only the partial pressures of the three most abundant species are shown in Figure 6.

Figures 5 and 6 show that the oxyhydroxide CrO$_3$(OH)$_2$(g) is the most abundant species in the vapour. Its abundance, and thereby also the chromium vaporization, increases if the H$_2$O partial pressure (Figure 5) and the Sr content in La$_{1-x}$Sr$_x$CrO$_3$ (Figure 6) is raised. It should be mentioned that the partial pressures of the chromium oxide species are independent from the H$_2$O partial pressure (Figure 5). They are only determined by the O$_2$ partial pressure.

The partial pressures over the chromium base alloy (7) exceed the corresponding pressures over La$_{1-x}$Sr$_x$CrO$_3$ by a factor of 140 to 10 (Figure 6). The factor decreases if the Sr content in La$_{1-x}$Sr$_x$CrO$_3$ is raised. The difference amounts to a factor of 50 for the composition La$_{0.85}$Sr$_{0.15}$CrO$_3$ which might be of practical interest.

4.3 Degradation Mechanisms by Chromium Vaporization

The mechanisms proposed by us for the explanation of the degradation of the electrical properties base on electrochemical reactions and are schematically shown in Figure 7. Chromium oxide or oxyhydroxide species with high chromium valence such
as CrO₂(OH)₂ vaporize from the interconnect surface and are transported in the gas phase to the cathode and the electrolyte. The species are reduced at the electrochemical active sites where they form Cr₂O₃(s) which inhibits the oxygen reduction necessary for the operation of SOFC and leads to polarization losses. More details on the degradation mechanisms proposed are given in Ref. 7.

The partial pressures of the chromium containing species determined in this work represent the source term for the chromium transport to the electrochemical active sites according to the mechanisms proposed. The decrease of the pressures caused by the use of a ceramic LaCrO₃ base interconnect (cf. Figure 3) causes a retardation of the Cr₂O₃ precipitation at these sites as compared to a metallic chromium base interconnect. A quantitative estimation (26) of the chromium transport in the flowing gas at the cathode side shows that a submicron layer of insulating Cr₂O₃ can be easily formed thereby deteriorating the cell operation if a metallic chromium base interconnect is used. It is assumed in the estimation that a stagnant gaseous boundary layer is formed adjacent to the alloy surface and that diffusion of the gaseous species through this layer into the turbulent flowing gas determines the chromium transport. The partial pressures over the alloy represent the starting concentration for the diffusion.

4.4 Formation of SrCO₃ in Interconnect Material

The values for the thermodynamic activity of SrO in La₁₋ₓSrₓCrO₃ are high (cf. Figure 4). The values can be used to compute the conditions for the formation of SrCO₃ in La₁₋ₓSrₓCrO₃ under a H₂/CO₂ atmosphere present at the anode according to the reaction:

\[
\text{SrO(s) + CO}_2(g) = \text{SrCO}_3(s), \quad [2]
\]

where SrO(s) means SrO bound in La₁₋ₓSrₓCrO₃. By using \(a(\text{SrO})=0.16\) for the thermodynamic activity of SrO in La₀.₈Sr₀.₂CrO₃, the data from the IVTANTHERMO data base [27], and \(p(\text{CO}_2)=0.1\) bar the following relation for the change of the Gibbs energy of the reaction Eq. [2] results:

\[
\Delta G_T/(\text{J mol}^{-1}) = -210617 + 175.7 \text{T/K}. \quad [3]
\]

Thermodynamic equilibrium, \(\Delta G_T=0\), is present for a temperature of 1199 K. This means that the formation of SrCO₃ is possible at temperatures below 1199 K; SrCO₃ is not stable at temperatures above this value.

First experiments were carried out with a sample of 506 mg of La₀.₈Sr₀.₂CrO₃ powder using thermogravimetry. No weight change was observed after annealing the sample at 1073 K under an atmosphere of 1 bar CO₂ over 15 h. The detection limit for the weight change at this experiment was 0.02 % of the sample weight. The measurements will be continued using higher temperatures than 1073 K, longer
annealing time periods than 15h, and H₂/CO₂ mixtures, as well as by cyclic variation of
the temperature.

ACKNOWLEDGMENT

The authors thank Prof. Steele for drawing their attention on the SrCO₃ formation in
interconnect material.

REFERENCES

1. N.Q. Minh, J. Am. Ceram. Soc., 76, 563 (1993).
2. A. Hammou, in Advances in Electrochemical Science and Engineering, H.
Gerischer and C.W. Tobias, Editors, Vol. 2, p. 87, Verlag Chemie,
Weinheim/Bergstr. (1992).
3. B.C.H. Steele, in Proc. 1st European Solid Oxide Fuel Cell Forum, Luzern,
Switzerland, Ulf Bossel, Editor, p. 375, Baden, Switzerland (1994)
4. S.C. Singhal, in Proc. 2nd International Symp. on Solid Oxide Fuel Cells, F.Gross,
P.Zegers, S.C. Singhal, O. Yamamoto, Editors, p. 25, Commission of the European
Communities, Luxembourg (1991).
5. G.M. Christie, P.H. Middleton, and B.C.H. Steele, J. European Cer. Soc. 14, 163
(1994).
6. W. Schäfer, H. Geier, G. Lindemann, and D. Stolten, in High Temperature
Electrochemical Behaviour of Fast Ion and Mixed Conductors, F.W. Poulsen, J.J.
Bentzen, T. Jacobsen, E. Skou, and M.J.L. Ostergard, Editors, p. 409, Risø National
Lab., Denmark, Roskilde (1993).
7. D. Das, M. Miller, H. Nickel, and K. Hilpert, in Proc. 1st European Solid Oxide
Fuel Cell Forum, Luzern, Switzerland, Ulf Bossel, Editor, p. 703, Baden,
Switzerland (1994).
8. W.J. Qudakkers, H. Greiner, and W. Köck, in Proc. 1st European Solid Oxide Fuel
Cell Forum, Luzern, Switzerland, Ulf Bossel, Editor, p. 525, Baden, Switzerland
(1994).
9. E. Batavi, K. Honegger, and R. Diethelm, in Proc. 6th IEA Workshop on Advanced
Solid Oxide Fuel Cells, p. 175, ENEA Rome, Rome, (1994).
10. B.C.H. Steele, personal communication, and Ref. 3.
11. H. Yokokawa, N. Sakai, T. Kawada, and M. Dokiya, J. Electrochem. Soc. 138,
1018 (1991).
12. S. Chen, Z. Hao, F. Li, and G. Zhou, Zhongguo Xitu Xuebao 5, 19 (1987).
13. A.M. Azad, R. Sudha, and O.M. Sreedharan, J. Less-Common Met. 166, 57 (1990).
14. See e.g. D.B. Meadowcroft and J.W. Wimmer, Ceram. Bull. 58, 610 (1979).
15. See e.g. R. Berjoan, A. Moise, M. Rivot, and J.P. Traverse, Sci. Ceram. 7, 343
(1973).
16. K. Hilpert, in Structure and Bonding, Vol. 73, "Noble Gas and High Temperature
Chemistry", M.J. Clarke, J.B. Goodenough, J.A. Ibers, C.K. Jorgensen, D.M.P.
Fig. 1. Phase diagram of the SrO-CrO$_3$-La$_2$O$_3$ system at 1873 K and low oxygen pressure, p(O$_2$) = 10$^{-9}$ bar, as well as compositions of the samples used in the vaporization studies, •, and phase diagram studies, ○, □.

Fig. 2. X-ray diffraction patterns after annealing LaSrCrO$_4$ at 1473 K at low oxygen pressure (p(O$_2$) = 10$^{-9}$ bar) (a) and in air (b)

[(La,Sr)$_2$CrO$_4$ ○; La$_2$O$_3$, △; (La,Sr)CrO$_3$, □; Sr$_{2.67}$Cr$_2$O$_{8.33}$, ▽)]
TABLE 1. Phase compositions, number of experimental points, \( n \), temperature range of the measurements, \( \Delta T \), and partial pressures over the \( \text{La}_{1-x}\text{Sr}_x\text{CrO}_3 \) samples of different compositions, \( x \), at 2000 K.

| Phase composition a) | \( x \) | Number of runs | \( n \) | \( \Delta T / K \) | \( p(i)/\text{Pa at 2000 K} \) |
|----------------------|------|---------------|------|----------------|---------------------------------|
| P                   | 0.10 | 2             | 20   | 1908 - 2127    | 0.24 0.16 0.025 0.046 4.4 \( 10^3 \) 9.5 \( 10^3 \) 7.4 \( 10^5 \) |
| P                   | 0.14 | 1             | 20   | 1770 - 2069    | 0.15 0.017 0.037 0.045 4.5 \( 10^3 \) 8.3 \( 10^3 \) 1.3 \( 10^4 \) |
| P                   | 0.15 | 1             | 18   | 1787 - 2090    | 0.44 0.035 0.046 0.067 5.1 \( 10^3 \) 1.1 \( 10^2 \) 5.7 \( 10^5 \) |
| P                   | 0.20 | 1             | 14   | 1866 - 2101    | 0.75 0.055 0.063 0.078 6.3 \( 10^3 \) 3.6 \( 10^3 \) 4.9 \( 10^5 \) |
| P                   | 0.22 | 2             | 43   | 1786 - 2091    | 0.30 0.043 0.087 0.056 6.6 \( 10^3 \) 3.1 \( 10^3 \) 1.9 \( 10^4 \) |
| P                   | 0.24 | 1             | 17   | 1877 - 2215    | 0.52 0.050 0.079 0.080 3.3 \( 10^3 \) - 8.4 \( 10^5 \) |
| P                   | 0.30 | 1             | 15   | 1840 - 2081    | 0.62 0.099 0.21 0.053 4.3 \( 10^3 \) 8.8 \( 10^4 \) 2.3 \( 10^4 \) |
| P + \( \text{La}_2\text{O}_3 \) | 0.11 | 2             | 36   | 1799 - 2115    | 0.10 0.012 0.031 0.055 4.1 \( 10^3 \) 1.5 \( 10^2 \) 1.5 \( 10^4 \) |
| P + \( \text{La}_2\text{O}_3 \) | 0.15 | 1             | 15   | 1891 - 2160    | 0.26 0.025 0.044 0.067 8.2 \( 10^3 \) 9.4 \( 10^3 \) 8.7 \( 10^5 \) |
| P + R                | 0.18 | 1             | 11   | 1908 - 2085    | 0.53 0.040 0.075 0.19 7.2 \( 10^3 \) 7.8 \( 10^3 \) 5.3 \( 10^5 \) |
| P + R                | 0.20 | 2             | 38   | 1819 - 2103    | 0.37 0.051 0.088 0.064 5.4 \( 10^3 \) 5.6 \( 10^3 \) 1.7 \( 10^4 \) |
| P + \( \text{Cr}_2\text{O}_3 \) | 0.17 | 1             | 17   | 1716 - 1981    | 3.7 0.80 2.3 0.047 1.9 \( 10^2 \) 2.4 \( 10^4 \) 4.3 \( 10^4 \) |
| P + \( \text{Cr}_2\text{O}_3 \) | 0.22 | 1             | 18   | 1759 - 2040    | 3.4 0.79 2.2 0.034 1.5 \( 10^2 \) 3.1 \( 10^4 \) 5.0 \( 10^4 \) |

a) P = Perovskite, R = Ruddlesden - Popper phase
Fig. 3. Partial pressures of the vapour species over the samples \{Cr_{2}O_{3} + La_{0.83}Sr_{0.17}CrO_{3}\} (a) and \{La_{2}O_{3} + La_{0.83}Sr_{0.17}CrO_{3}\} (b)

Fig. 4. Thermodynamic activities of the components in La_{1-x}Sr_{x}CrO_{3}, x = 0 - 0.3, at 2000 K

Fig. 5. Composition of the equilibrium vapour over LaCrO_{3}(s) at 1223 K in air for different H_{2}O partial pressures
Fig. 6. Composition of the equilibrium vapour over La$_{x}$Sr$_{y}$CrO$_{3}$ of different Sr content at 1223 K in humid air (p(H$_2$O) = 0.02 bar)

Fig. 7. Schematic representation of the Cr transport by the formation of CrO$_2$(OH)$_2$(g)