A/B-Ratio and Transport Properties of $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$ Perovskites

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Abstract. The perovskites $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$ and $(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$ have been investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM) and electrical conductivity relaxation (ECR). This system was chosen in order to investigate the influence of cation vacancies on the transport properties in the materials. From ECR-measurements it is concluded that no difference in the chemical diffusion coefficient for oxide ions between the two samples can be found. The activation energy for the chemical diffusion coefficient has been found to be $107 \pm 5 \, kJ \, mol^{-1}$. However, the surface exchange coefficient differs between the two samples. The Co-rich sample has a significantly higher surface exchange coefficient than the A/B-stoichiometric sample. For both samples the surface exchange coefficient was almost independent of the temperature. At all temperatures the Co-rich sample had a significantly higher electrical conductivity. The difference in electrical conductivity between the two samples diminished when going to higher temperatures. Both materials can be assigned to a single phase hexagonal perovskite. An annealed sample of $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$ did however contain an unidentified secondary phase on the surface.

Keywords: A/B-ratio, oxide ion conductivity, electrical conductivity relaxation, cation vacancies, perovskites, lanthanum strontium cobaltites

1. Introduction

Perovskites have the general chemical formula ABO_3 where A is a large metal ion, typically a rare earth metal and B is a small cation typically a transition metal. Many studies have been carried out on the catalytic properties, oxide ion and electronic conductivity and their dependence on both A and B elements. Few studies have investigated the effect of varying the A/B-ratio. Kharton et al. investigated the A-site deficient perovskites $Sr_{1-y}Fe_{0.8}Ti_{0.2}O_{3-\delta}$ ($y = 0$–0.06) and found that at low temperature the electrical conductivity varied strongly with the A/B-ratio [1]. The oxide ion conductivity varied with the A-site deficiency and went through a maximum for the composition $Sr_{0.97}Fe_{0.8}Ti_{0.2}O_{3-\delta}$. This maximum in conductivity was assigned to an increasing cation disorder which suppresses long-range ordering in the oxide sublattice. Kovalevsky et al. [2] investigated the oxygen permeation through membranes of $La_{0.35}Sr_{0.65-y}CoO_{3-\delta}$

($y = 0$–0.1). The oxygen flux was dependent on the A/B-ratio however, in this case the oxygen permeation diminished when lowering the A/B-ratio from 1 to 0.9. Morin et al. [3] made a thorough investigation of the phase stability of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and found that the perovskite phase was only stable for a very small deviation from unity ($0.997 < A/B < 1.003$). Here we report on effects of varying the A/B-ratio with studies on $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$ and $(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$. Mineshige et al. [4] measured that at low temperature the electrical conductivity was very sensitive to the strontium doping in the vicinity of a doping of 0.15. The large variation in electrical conductivity will perhaps also be reflected in other physical properties such as the oxygen chemical diffusion coefficient, D_{Chem} or the oxygen surface exchange coefficient, k_{Ex}. D_{Chem} and k_{Ex} have been measured using electrical conductivity relaxation (ECR). The samples have also been examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Theory

In ECR the electrical conductivity is followed after an abrupt change in the oxygen partial pressure. When changing the oxygen partial pressure the perovskite will adjust its oxygen stoichiometry according to Eq. (1):

$$2\,O_O^\times \rightarrow O_2 + 2\,V_O^{\bullet\bullet} + 4e'$$ (1)

where $V_O^{\bullet\bullet}$ is an oxide ion vacancy, $O_O^\times$ is an oxide ion on a regular site, e' is an electron. Materials in the system $(La,Sr)CoO_{3-\delta}$ are generally known to be *p*-type conductors [5, 6]. Upon vacancy formation electrons are transferred to a partially filled conduction band thereby lowering the electron hole concentration resulting in a decrease in the conductivity. The electro-neutrality condition can be written:

$$3\left[V_A^{'''}\right] + \left[Sr_{La}^{'}\right] = 2\left[V_O^{\bullet\bullet}\right] + p$$ (2)

p is the electron hole concentration, $[V_A^{'''}]$ is the concentration of vacancies on the A-site and $[Sr_{La}^{'}]$ is the strontium doping level. Since the electrical conductivity is assumed proportional to the electron hole concentration, the electrical conductivity can be correlated to the oxide ion vacancy concentration.

The investigated samples all have a well defined rectangular bar shape and well polished surfaces. The change in electrical conductivity can therefore be correlated to diffusion of oxide ions in the samples with a first order surface reaction. According to Carslaw and Jaeger [7] the solution to the 2-dimensional diffusion problem can be described using Eq. (3).

$$\frac{\sigma_\infty - \langle\sigma(t)\rangle}{\sigma_\infty - \sigma_0} = \sum_{n=1}^{\infty} \frac{2L_x^2 \exp\left(\frac{-\beta_{n,x}^2 D_{Chem}t}{l_x^2}\right)}{\beta_{n,x}^2\left(\beta_{n,x}^2 + L_x^2 + L_x\right)}$$
$$\times \sum_{n=1}^{\infty} \frac{2L_y^2 \exp\left(\frac{-\beta_{n,y}^2 D_{Chem}t}{l_y^2}\right)}{\beta_{n,y}^2\left(\beta_{n,y}^2 + L_y^2 + L_y\right)}$$
(3)

σ_∞, σ_0, and $<\sigma(t)>$ are the electrical conductivities at infinite time, zero time and time t, respectively. $L_x = l_x k_{Ex}/D_{Chem}$ and $\beta_{n,x}$ is the *n*'th positive solution to the equation $\beta_{n,x}\tan\beta_{n,x} = L_x$. A 2-dimensional solution is used since the conductivity is measured over a short distance in the middle of a long sample. The chemical diffusion coefficient and surface exchange coefficient were determined by fitting Eq. (3) to the change in conductivity following an abrupt step in the oxygen partial pressure.

3. Experimental

In order to prepare perovskites with a precise stoichiometry care must be taken in the synthesis. The glycine nitrate route was used to synthesize the materials as described by Chick et al. [8]. This synthesis rapidly produces a powder with a small grain size (<1 μm), which makes it suitable for preparation of dense samples. The aqueous nitrates were prepared from $La(NO_3)_3 \cdot 6H_2O$, $SrCO_3$ and $Co(OH)_2$ using high purity water ($\rho = 18.2$ MΩ cm) and nitric acid. The raw materials all had a purity of 99.9% or better. The concentration of the metal nitrates solutions was carefully determined with an uncertainty less than 0.5%. Within the uncertainty the Co-rich sample must therefore be A-site deficient. For the A/B-stoichiometric sample it is not known if the sample is A- or B-site deficient. Dense samples of the two perovskites were prepared by using PVA 100.000 as binder. Samples were pressed uniaxially followed by isostatic pressuring at 325 MPa. Samples were sintered at 1200°C for 4 h and at 1175°C for 16 h.

Samples for ECR were cut from larger samples and polished with SiC-paper #1000 followed by #4000. The geometrical density compared to the XRD-density was 95% and 100% for the Co-rich sample and the A/B-stoichiometric sample respectively. Samples for XRD, SEM and ECR were annealed in pure oxygen for 3 days at 1000°C followed by 1 day at 650°C. Slow ramp rates were used in order to make sure that the samples had an oxygen stoichiometry as close as possible to 3 when cooled to room temperature. The bulk of a Co-rich sample that had not been annealed was also investigated in XRD, to see if secondary phases could be detected in the bulk.

4. Results and Discussion

4.1. XRD and SEM Analysis

Figure 1 shows the XRD-pattern for the bulk $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$-sample. The bulk Co-rich sample is a hexagonal single phase perovskite.

Table 1. Lattice parameters for the three investigated samples. A. surf. = annealed surface at 1000°C for 72 h followed by 24 h at 650°C.

	a-axis (Å)	*c*-axis (Å)
$(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$, Bulk	5.4453	13.1507
$(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$, A. surf.	5.4478	13.1549
$(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$, A. surf.	5.4469	13.1461

The surface of the annealed $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$-sample (shown as the inserted XRD-pattern in Fig. 1) contained foreign phases. These phases have at present not been identified. The XRD-pattern of $(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$ was also assigned to a hexagonal single phase perovskite. Table 1 gives lattice constants for the investigated samples. It is observed that the Co-rich unit cell has contracted a little when compared to the A/B-stoichiometric unit cell. The XRD-results for the A/B-stoichiometric unit cell are in good agreement with measurements on the same composition by Mineshige et al.[4].

The samples were also investigated in SEM after the annealing. No secondary phases were present in the A/B-stoichiometric sample, while on the Co-rich perovskite Co-oxide particles were observed at the grain boundaries. The distribution of Co-particles varied strongly across the sample, but of the total surface area less than 1% was covered with Co-particles. The Co-particles were approximately 1 μm in diameter. No impurities except for trace amounts of Zr were detected which originates from the ball milling. Even though no La- or Co-rich phases were observed on the A/B-stoichiometric sample it cannot be excluded that such phases are present but in a very small concentration, that could not be observed using SEM or XRD.

4.2. Electrical Conductivity

Figure 2 shows the electrical conductivity as function of the temperature for the two samples. For both samples a gradual transition from semi-conducting to metallic conductivity is observed. The Co-rich sample has been corrected for the 5% porosity [9]. Mineshige et al. [4] also measured the conductivity of $La_{0.85}Sr_{0.15}CoO_{3-\delta}$. The values by Mineshige are in agreement with the A/B-stoichiometric sample at room temperature. At higher temperatures we measure a maximum conductivity of 1834 Scm^{-1}. Mineshige measures a maximum conductivity of approximately 1500 Scm^{-1} for his sample. The reason for this rather large discrepancy is unknown. We estimate the uncertainty on the electrical conductivity to be not more than 5%.

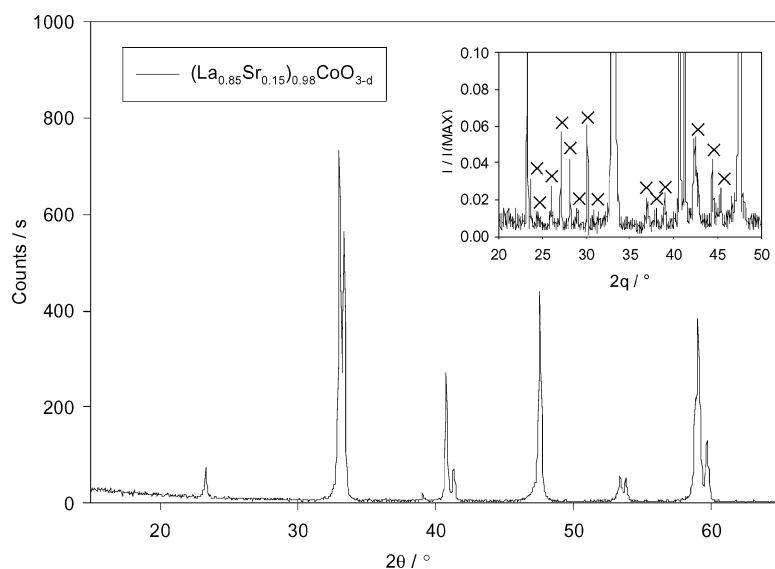At all temperatures the Co-rich sample has a significant higher conductivity than the stoichiometric

Fig. 1. XRD-pattern of $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$—for both a bulk sample and the surface of an annealed sample (inserted XRD-pattern). Several impurity phases (marked with a '×') are observed in the XRD-pattern of the surface of the annealed Co-rich sample.
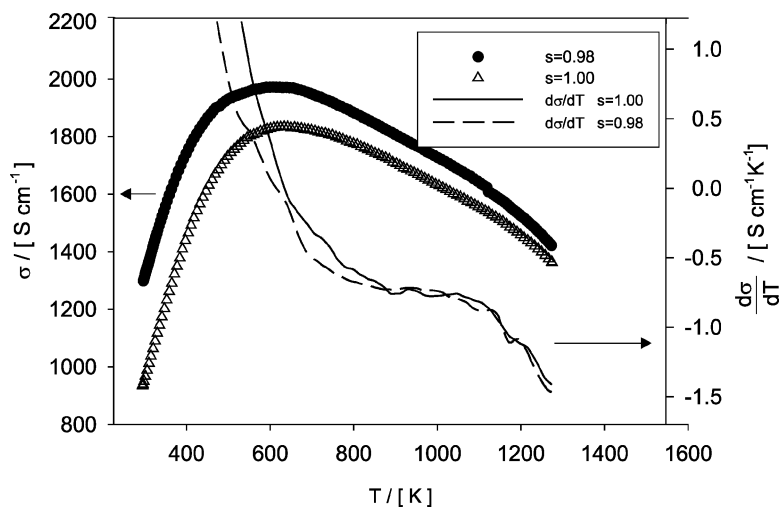
Fig. 2. Electrical conductivity of $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$ as function of the temperature (left axis). Also shown is the derivative of the electrical conductivity with respect to the temperature (right axis).

sample. Since the electrical conductivity of the Co-rich sample is higher than the A/B-stoichiometric sample, the A-site vacancies have most likely been compensated by electron holes at low temperatures according to Eq. (2). At temperatures above 1100 K the difference in electrical conductivity becomes smaller, which indicate that the difference in the electron-hole concentration also diminishes, assuming a constant electronhole mobility. One possibility is that the Co-rich sample compensates by creating more oxide ion vacancies at higher temperatures according to Eq. (2).

Also shown on the figure is the derivative of the conductivity with respect to the temperature (right axis). When the material starts to loose oxygen at approximately 1100 K[10] this is clearly reflected in the derivative curve as a decrease below -0.7 Scm^{-1} K^{-1}.

4.3. Electrical Conductivity Relaxation

Figures 3 and 4 show the measured values of D_{Chem} and k_{Ex} as function of the oxygen partial pressure for both polished samples at 1123, 1173, 1223 and 1273 K. The data in Figs. 3 and 4 are from reduction steps, and the data are depicted as function of the most reducing oxygen partial pressure. When fitting the measured relaxations it was found that at low oxygen partial pressure (pO$_2$ < 0.003 atm) the surface exchange reaction is rate determining. A minimum value of the chemical

diffusion coefficient can always be found by applying an infinite high surface exchange coefficient, but the uncertainty on the diffusion coefficient is very large at the lowest oxygen partial pressures (of the order 100%). However a minimum value can always be found. Since k_{Ex} is the rate determining factor the uncertainty has been estimate as less than 10% at the lowest oxygen partial pressure. At high oxygen partial pressures (pO$_2$ > 0.01 atm) the surface exchange reaction is fast, resulting in a large uncertainty on k_{Ex} and a small uncertainty on D_{Chem}. A minimum value of k_{Ex} can always be found by applying an infinite high value of D_{Chem}. The uncertainty on D_{Chem} is less than 15% at the highest oxygen partial pressures. The k_{Ex}-values at pO$_2$ > 0.01 atm plotted on Fig. 4 are a linear extrapolation using the tendency of k_{Ex} observed at pO$_2$ < 0.01 atm. At 0.003 atm < pO$_2$ < 0.01 atm the sample is in a mixed regime, where it is possible to determine D_{Chem} and k_{Ex} with a small uncertainty. Similar behavior has also been observed by tenElshof et al. on $La_{1-x}Sr_xFeO_{3-\delta}$-compounds [11].

At 1273 K the chemical diffusion coefficient is equal for the two samples within the uncertainty of the measurements. At the temperatures 1173 and 1123 K the chemical diffusion coefficient for the Co-rich sample seems to be higher than for the A/B-stoichiometric sample. Generally, a relatively constant value of D_{Chem} is observed when changing the oxygen partial pressure. The values at high oxygen partial pressures are in good agreement with measurements made by van der
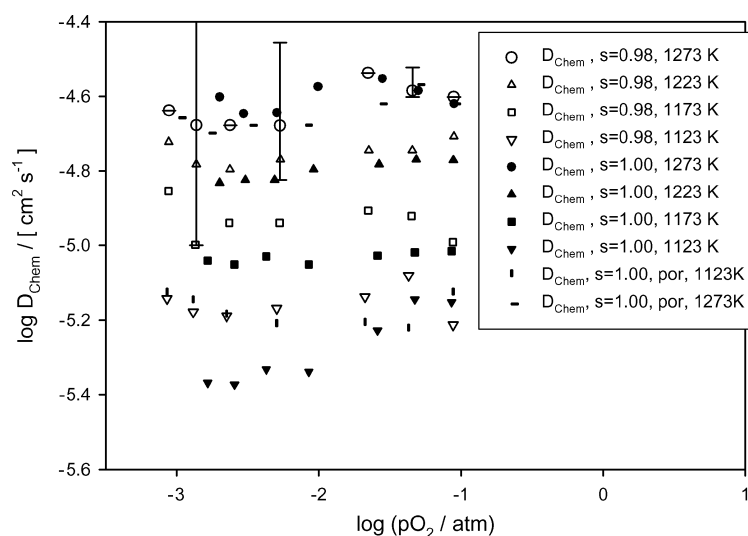
Fig. 3. Measured D_{Chem}-values for the investigated $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$-compositions. Values of D_{Chem} are plotted as function of the most reducing oxygen partial pressure. The legend "por" is for the A/B-stoichiometric sample with a porous surface layer. The uncertainty on the measurements is shown for $s = 0.98$ at $T = 1273$ K.
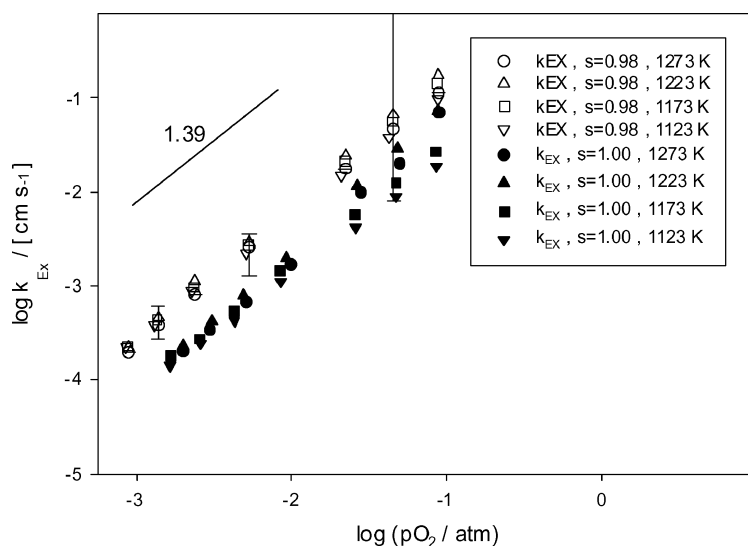

Fig. 4. Measured k_{Ex}-values for the investigated $(La_{0.85}Sr_{0.15})_sCoO_{3-\delta}$-compositions. Values of k_{Ex} are plotted as function of the most reducing oxygen partial pressure. Error bars are shown for: $s = 0.98$ at $T = 1273$.

Haar et al. [12] who investigated $La_{0.8}Sr_{0.2}CoO_{3-\delta}$. We have previously observed that there is a strong correlation between D_{Chem} and k_{Ex} when fitting relaxation curves, especially when k_{Ex} becomes small. In order to clarify whether there is a correlation between D_{Chem} and k_{Ex} the A/B-stoichiometric sample was added a porous surface coating of $(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$. A porous layer is expected to enhance the surface ex-

change reaction, thereby decreasing the uncertainty on D_{Chem}. The A/B-stoichiometric sample with a porous surface layer was investigated using ECR. It was found that the chemical diffusion coefficient was within the uncertainty exactly the same as for the Co-rich sample at 1123K. On Fig. 3 only D_{Chem} measurements at 1123 and 1273 K are shown for the sample with the porous surface layer. The surface exchange coefficient

measured with a porous surface layer was almost the same as k_{Ex} measured for the Co-rich perovskite. There have been no attempts to optimize the porous surface layer. The difference in D_{Chem} between the two polished samples in Fig. 3 is therefore not a real effect but an artifact due to a small k_{Ex} value. No change in the chemical diffusion coefficient between the two investigated compounds has therefore been found. The activation energy for the chemical diffusion coefficient has been found to be 107 ± 5 kJ/mol at $pO_2 = 0.022$ atm.

The surface exchange coefficients for the two polished samples are observed to be substantially different as seen on Fig. 4. The Co-rich cobaltite has a significant higher k_{Ex}-value than the A/B-stoichiometric sample. It is also observed that for both samples the same slope is observed and that in the temperature interval 1123–1173 K the surface exchange coefficient is virtually independent of the temperature. The large difference in k_{Ex} between the two samples can be due to cation-vacancies on the surface of the Co-rich perovskite, which enhances the surface reaction. A second possibility is that the secondary phases present on the Co-rich cobaltite catalyzes the oxygen reduction. Finally, the Co-rich sample must contain more oxide ion vacancies according to the temperature dependence of the electrical conductivity. These extra oxide ion vacancies if present on the surface will most likely increase the rate of oxygen incorporation into the perovskites [13].

5. Conclusion

A large difference on the oxygen surface exchange reaction between samples of annealed $(La_{0.85}Sr_{0.15})_{0.98}CoO_{3-\delta}$ and $(La_{0.85}Sr_{0.15})_{1.00}CoO_{3-\delta}$ has been observed. The Co-rich sample had a markedly higher k_{Ex}-value, which may be caused by the creation of cation-vacancies on the surface. Cation vacancies on the surface could be speculated to enhance the surface exchange rate. From electrical conductivity measurements it seems reasonable to conclude that the A/B-stoichiometric sample contains more oxide ions vacancies. If these oxide ion vacancies take part in the oxygen incorporation, an increase on the surface will enhance the surface exchange reaction. A third possibility is that the secondary phases that have been observed on the surface of the annealed Co-rich sample using XRD and SEM have a very high catalytic effect

for oxygen reduction. The annealed surface of the A/B-stoichiometric sample could be assigned to a hexagonal single phase perovskite.

Using a porous surface coating for the A/B-stoichiometric sample it has been found that within the uncertainty no difference in the chemical diffusion coefficient can be observed between the two samples. The activation energy for D_{Chem} has been found to 107 $\pm$ 5 kJ/mol (at $pO_2 = 0.022$ atm).

The electrical conductivity for the two samples was within the uncertainty equal at temperatures above 620 K. Below 620 K the Co-rich sample had a significantly higher electrical conductivity. This is believed to be caused by that the creation of A-site vacancies in the Co-rich sample has been compensated by the formation of electron-holes at low temperature. At higher temperatures the A-site vacancies are compensated more and more by oxide ion vacancies, thereby reducing the electron hole concentration.

References

1. V.V. Kharton, A.V. Kovalevsky, E.V. Tsipis, A.P. Viskup, E.N. Naumovich, J.R. Jurado, and J.R. Frade, *Journal of Solid State Electrochemistry*, **7**, 30 (2002).
2. A.V. Kovalevsky, V.V. Kharton, V.N. Tikhonovich, E.N. Naumovich, A. A. Tonoyan, O.P. Reut, and L.S. Boginsky, *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, **52**, 105 (1998).
3. F. Morin, G. Trudel, and Y. Denos, *Solid State Ionics*, **96**, 129 (1997).
4. A. Mineshige, M. Inaba, T.S. Yao, Z. Ogumi, K. Kikuchi, and M. Kawase, *Journal of Solid State Chemistry*, **121**, 423 (1996).
5. M.H.R. Lankhorst, *Thermodynamic and Transport Properties of Mixed Ionic-Electronic Conducting Perovskite-Type Oxides* University of Twente, 1997).
6. J. Mizusaki, J. Tabuchi, T. Matsuura, S. Yamauchi, and K. Fueki, *Journal of the Electrochemical Society*, **136**, 2082 (1989).
7. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, 2nd. edn. (Clarendon Press, 1959).
8. L.A. Chick, G.D. Maupin, G.L. Graff, L.R. Pederson, D.E. McCready, and J.L. Bates, in *Mat. Res. Soc. Symp. Proc.*, **249**, 159 (1992).
9. S. Linderoth, N. Bonanos, K.V. Jensen, and J.B. Sørensen, *Journal of The American Ceramic Society*, **84**(11), 2652 (2001).
10. J. Mizusaki, Y. Mima, S. Yamauchi, K. Fueki, and H. Tagawa, *Journal of Solid State Chemistry*, **80**, 102 (1989).
11. J.E. tenElshof, M.H.R. Lankhorst, and H.J.M. Bouwmeester, *Solid State Ionics*, **99**, 15 (1997).
12. L.M. van der Haar, M.W. den Otter, M. Morskate, H.J.M. Bouwmeester, and H. Verweij, *Journal of the Electrochemical Society*, **149**, J41 (2002).
13. J.A. Kilner, R.A. DeSouza, and I.C. Fullarton, *Solid State Ionics*, **86–88**, 703 (1996).