High-temperature electrical conductivity of $Sr_{0.7}La_{0.3}FeO_{3-\delta}$

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Abstract

The electrical properties of the lanthanum-doped strontium ferrite $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ are studied within the temperature range 750–950°C and the oxygen partial pressure range between 10^{-19} and 0.5 atm. The ferrite undergoes a transition from perovskite-like to brownmillerite-like structure at an oxygen pressure of about 10^{-4} atm in the studied temperature range. The observed pressure and temperature dependencies of the conductivity in the brownmillerite-like form of the ferrite are related to the transition of the electron conductivity from the intrinsic regime, which is governed by the band gap of about 2 eV, to the extrinsic regime, which is controlled by the extra-stoichiometric oxygen in the brownmillerite-like phase. The brownmillerite-like phase is shown to be a mixed conductor with the oxygen conductivity level rising to about 0.3 S/cm at about 900°C. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years. the study of oxide materials having both electron and oxygen ion conductivity has received considerable attention, since they hold promise for use as oxygen semipermeable membranes in reactors for methane to syngas conversion. One particular research focus has been on alkaline earth-doped perovskite-like cobaltites where oxygen semipermeability is sufficiently high for the application. Unfortunately, the thermodynamic stability of the cobaltites is unsatisfactory. Alternative and more stable oxides are perovskite-like ferrites. The lanthanum-doped strontium ferrite $Sr_{1-x}La_xFeO_{3-\delta}$ was shown to have substantial values of both p- and n-type electron [1–3] and oxygen-ion [4–6] components of conductivity in the high-temperature range and at oxygen partial pressure p_{O_2} above 10^{-4} atm. In contrast to these reports, the data on conducting properties of the ferrite at smaller partial pressure of oxygen are scarce [7]. It is known only that the p-type electron conductivity is eventually replaced by the n-type electron conductivity at sufficiently low p_{O_2} [1–3]. Also, the question remains whether

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oxygen ion conductivity at low oxygen pressure is of the same level as in the high-pressure range. The present study was directed at measuring electrical conductivity in $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ at 750–950°C in the extended range of oxygen partial pressure 10^{-19}–0.5 atm, evaluation of the oxygen ion contribution, and elucidation of the mechanism of conductivity at large oxygen deficiency.

2. Experimental

The powder specimen $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ was made by a solid-state reaction method with appropriate amounts of high-purity grade, La_2O_3, Fe_2O_3 and $SrCO_3$. The starting reagents were calcined for 10 h at 600°C and weighed in a dry box. The X-ray powder diffraction was used to confirm the single-phase cubic perovskite with the elementary unit parameter $a = 3.8728 \pm 0.0002$ Å. The resulting powder was pressed with a 1-kbar load into pellets 20 mm in diameter and 2 mm thick. The pellets were sintered at 1200°C in air for 10 h. Densities were about 93% of theoretical. Rectangular bars $2 \times 2 \times 18$ mm were cut from the sintered pellets for electrical measurements. One specimen, equipped with butt electrodes and thermocouples, was used for measurements of thermopower α. The temperature gradient along the sample was about 15 K/cm. Another specimen was used in four-probe measurements of the d.c. conductivity σ. The current leads were tightly wound to the sample at 16 mm spacing, whereas the spacing between potential probes was 10 mm. The specimen was placed perpendicular to the specimen for thermopower measurements so that the temperature gradient along the sample was zero. The measurements were carried out in a cell utilizing oxygen sensing and pumping properties of cubically stabilized zirconia as described elsewhere [8]. The cell was filled with a 50% O_2, 50% CO_2 gas mixture in the beginning of the experiment and sealed. A typical value of the pump current necessary to maintain a desirable oxygen pressure inside the cell did not exceed 0.5 mA. The electrical parameters were measured with a high-precision voltmeter Solartron 7081. The experimental data points were collected upon achievement of equilibrium between the sample and oxygen gas in the ambient. The equilibrium

state was assumed to be attained when changes in the logarithm of the conductivity did not exceed 0.1%/min and changes in thermopower did not exceed 0.001 μV/min. The measurements were carried out in the isothermal runs. Thermopower data were corrected for the contribution of the platinum leads [9].

3. Results and discussion

The isothermal plots of the logarithm of the conductivity and thermopower in $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ versus the logarithm of oxygen partial pressure are shown in Fig. 1. The complicated character of the curves may reflect changes both in the oxygen content and crystalline structure of the ferrite. In the high-pressure limit where crystalline structure is that of the cubic perovskite, the thermopower sign is positive in accord with the p-type conductivity. Also, the conductivity increases, whereas thermopower simultaneously decreases with the pressure increase. Considering that $\sigma \sim [h^+]$ and $\alpha \sim \ln(1/[h^+])$, where $[h^+]$ is concentration of electron holes, these changes reflect the increase in the amount of hole carriers with pressure, that is, with the increase of the oxygen content in the ferrite. The temperature dependence of both conductivity and thermopower is indicative of metallic-like behavior. The pressure decrease below about 10^{-4} atm results in appearance of nearly flat portions on the isothermal plots of conductivity and thermopower. However, metallic-like character of conductivity remains preserved. X-ray diffraction patterns of the specimens quenched from the values of oxygen pressure and temperature corresponding to flat portions on the conductivity curves confirm a crystalline structure related to brownmillerite. Therefore, the changes in electrical properties at about 10^{-4} atm in the studied temperature range reflect a structural transition. The elementary unit parameters $a = 5.498$, $b = 11.862$ and $c = 5.569$ Å of the quenched specimens are found in good correspondence with the data for $Sr_2LaFe_3O_8$ given in Ref. [10]. The structure of $Sr_2LaFe_3O_8$ can be viewed as the alternation along the b-axis of layers of iron–oxygen tetrahedra, where oxygen vacancies are ordered along the c-axis, and layers of iron–oxygen octahedra (Fig. 2). At a further de-
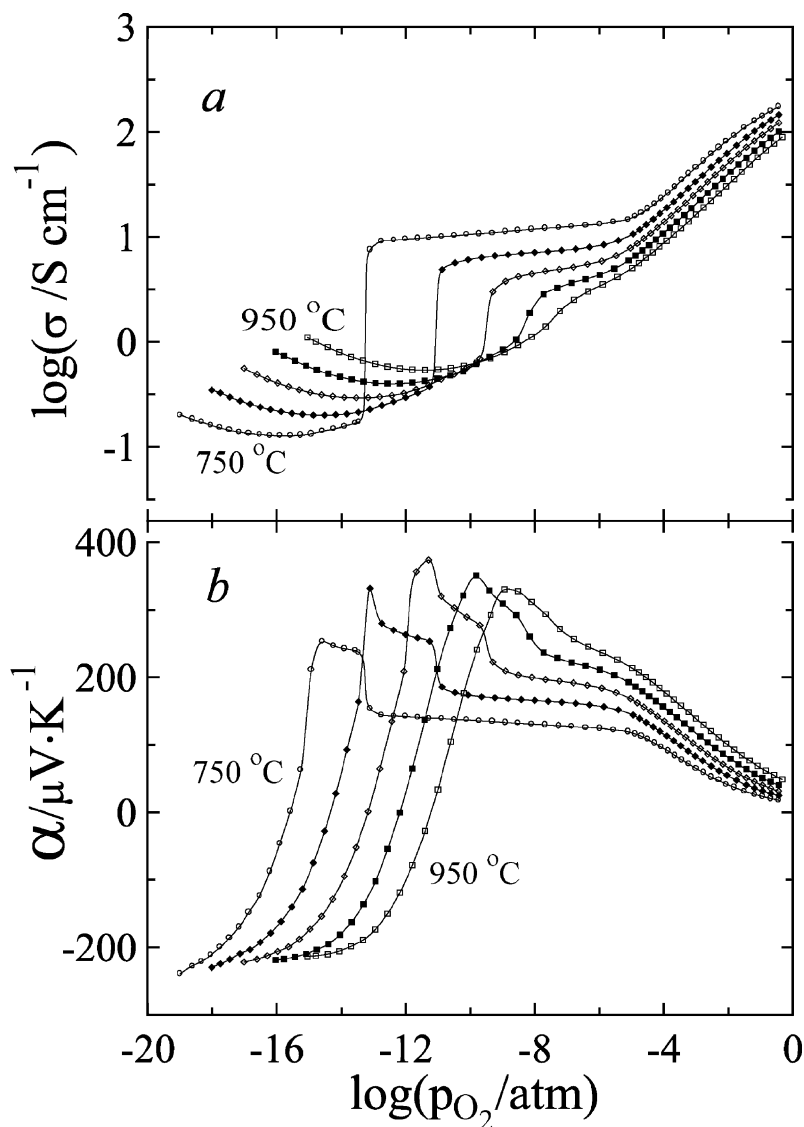
Fig. 1. The isothermal plots of the logarithm of the conductivity (a) and thermopower (b) versus the logarithm of partial pressure of oxygen. The temperature step between isotherms is 50°C.

crease in the pressure, thermopower increases to more positive values. Then, thermopower decreases, approaches zero and changes to negative values with the pressure decrease. The behavior of the conductivity isotherms in the same pressure range is characterized by sharp drops followed by flat minima at p_{O_2}'s corresponding to zero values of thermopower. At a further decrease in the pressure, conductivity begins to increase. The X-ray of the specimen quenched

from 850°C to room temperature at $p_{O_2} = 10^{-15}$ atm reveals the same characteristic pattern of the $Sr_2LaFe_3O_8$ phase (Fig. 3). It is possible therefore that the jumps on the isotherms of thermopower and conductivity are mainly related to changes in the electronic subsystem of the oxide. This conclusion is supported by the transition to semiconductor-like behavior in the temperature dependencies of conductivity and thermopower as the pressure decreases.
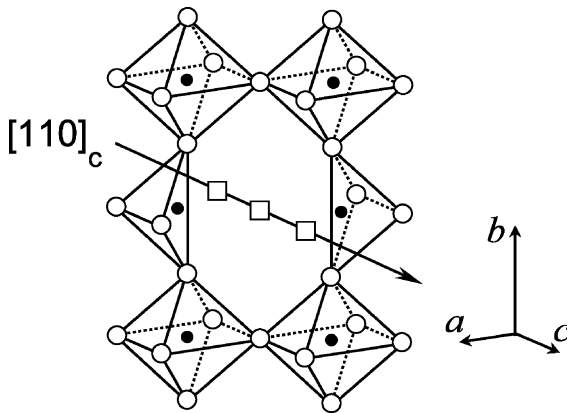
Fig. 2. A sketch of the crystalline structure of the ferrite $Sr_2LaFe_3O_8$ showing layers of the iron–oxygen octahedra and layers of the iron–oxygen tetrahedra with tunnels formed by ordered oxygen vacancies. ● —Iron ion; ○—oxygen ion; □—oxygen vacancy.

3.1. Oxygen ion conductivity

The measured values of the minimal conductivity for $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ in the semiconductor-like regime, that is, in the low-pressure range, are about an order of magnitude larger than the values found at comparable temperatures in specimens with smaller strontium content $Sr_{1-x}La_xFeO_{3-\delta}$, where $0.75 \leq x \leq 1$ [1,2]. At the same time, the obtained data are very close to the results given in the study of the samples with $x = 0.2$ and 0.4 [3]. It was shown in Refs. [1,2] that the lanthanum-rich ferrite is a band-gap semiconductor and the total conductivity is the sum of hole- and electron-like contributions changing with pressure as $\sigma_p \sim p_{O_2}^{+1/4}$ and $\sigma_n \sim p_{O_2}^{-1/4}$, respectively. Analogously, Kim et al. [3] accepted a presence of the electron and hole contributions only in their analysis of the conductivity in the strontium-rich ferrite. However, this supposition was not verified. Larger values of the minimal conductivity in the strontium-rich ferrite compared to the ones in lanthanum-rich ferrite can be related either to a band gap considerably smaller than in the lanthanum-rich compositions or to appearance of an additional contribution from the other charge carriers, that is, oxygen ions. Generally, the decreased value of the band gap may result in the electron–hole disorder domi-
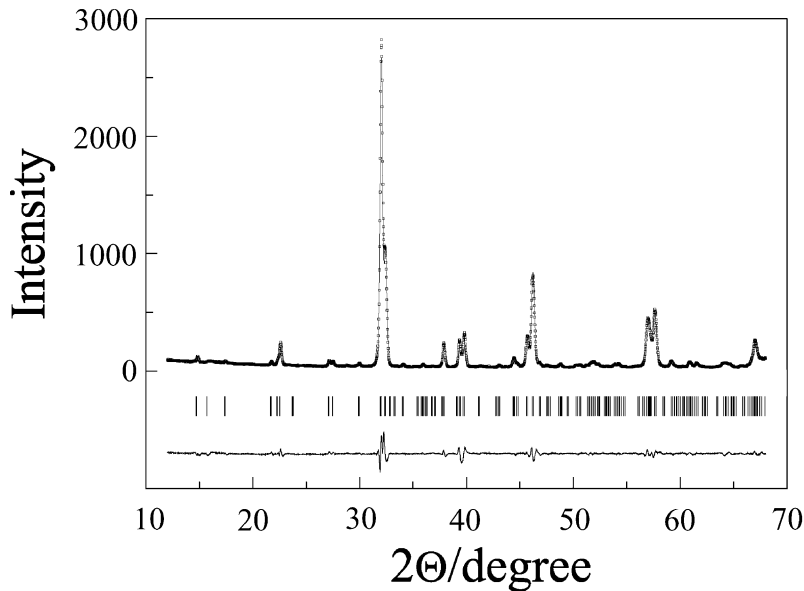

Fig. 3. The X-ray (CuK_α) diffraction data and Rietveld refinement profile for the ferrite $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ quenched from 850°C to room temperature at $p_{O_2} = 10^{-15}$ atm. The refinement was carried out with the use of structural data for $Sr_2LaFe_3O_8$ [10]. Dots are the raw observed data. The solid line is the calculated profile. Tick marks below the profile mark positions of all allowed reflections. The difference between the observed and calculated profiles is plotted at the bottom in units of difference divided by estimated standard deviation (which is the square root of the observed counts).

Table 1
Calculated values for the conductivity parameters in $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ at different temperatures

Parameter	T (°C)				
	950	900	850	800	750
A	3.4×10^{-1}	2.6×10^{-1}	1.9×10^{-1}	1.4×10^{-1}	9.0×10^{-2}
B	1.3×10^{-4}	5.4×10^{-5}	2.0×10^{-5}	6.6×10^{-6}	2.0×10^{-6}
C	7.5×10^{1}	9.6×10^{1}	1.2×10^{2}	1.5×10^{2}	1.8×10^{2}

nating over other processes of defect formation and in flat minima on the conductivity isotherms. However, estimations of the band gap in the specimens with $x = 0.2$, 0.4 [3] and $0.75 \leq x \leq 1$ [1,2] give the value of about 2 eV and are practically independent of the relative amount of strontium to lanthanum. Therefore, it is necessary to take into account the oxygen ion contribution for the correct description of conductivity in the ferrite $Sr_{1-x}La_xFeO_{3-\delta}$ with large strontium content at low oxygen pressure.

The analysis of the pressure dependencies of the conductivity isotherms near the minima results in the ordinary expression for a mixed, oxygen ion–electron conductor

$$\sigma(T, p_{O_2}) = A(T) + B(T) p_{O_2}^{-1/4} + C(T) p_{O_2}^{+1/4},$$
(1)

where $A(T)$, $B(T)$ and $C(T)$ are temperature-dependent parameters related to the ion, electron and hole components of the conductivity, respectively. The values of these parameters at different temperatures were found by fitting Eq. (1) to experimental isotherms of conductivity in Fig. 1 in the pressure range of semiconductor-like behavior (Table 1). The comparison of the calculated total conductivity with experimental data points is shown in Fig. 4. The temperature dependence of the derived ion conductivity is shown with Arrhenius coordinates in Fig. 5. It is seen that the ion conductivity increases with temperature and the activation energy is equal to 0.8 eV. This value is smaller than the activation energy 1.1 eV for the ion conductivity in the brownmillerite ferrite $SrFeO_{2.5\pm\delta}$ [8] and, therefore, the level of the oxygen ion conductivity is somewhat larger in $Sr_{0.7}La_{0.3}FeO_{3-\delta}$. It is seen from Fig. 5 that the oxygen ion conductivity in the brownmillerite-like phase of $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ achieves a value of about 0.2–0.3 S/cm at 850–900°C, which is larger than
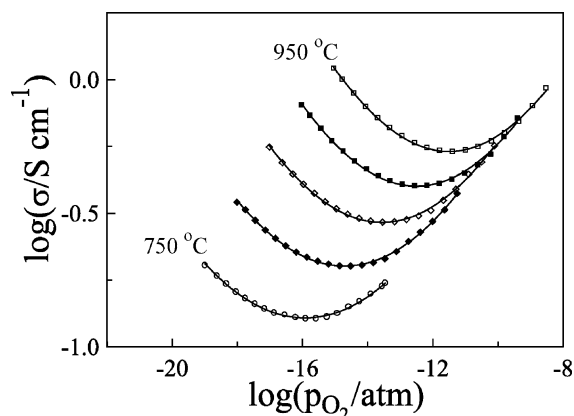

Fig. 4. Comparison of the experimentally measured total conductivity (squares) with the calculated conductivity (solid lines) in the low-pressure range. The temperature step between isotherms is 50°C.
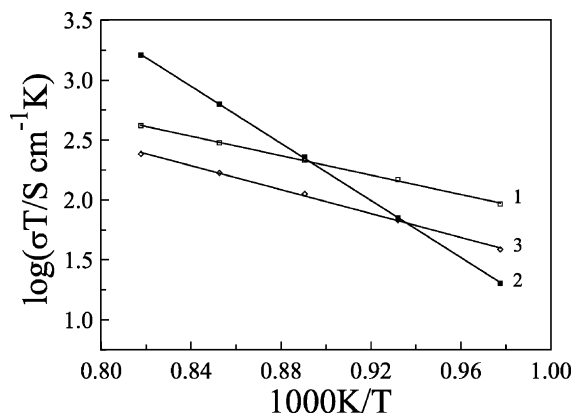

Fig. 5. The Arrhenius plots for partial contributions and for minimal conductivity. Solid lines show linear fit to the data. 1—The oxygen ion contribution corresponding to temperature dependence of $\log(AT)$. The activation energy is 0.8 eV. 2—The electron contribution calculated from values of $\log(\sigma_n T)$ at $p_{O_2} = 10^{-16}$ atm. The activation energy is 2.35 eV. 3—The temperature dependence of $\log(\sigma_{min} T)$. The activation energy is 1.0 eV.

the ion conductivity in other known electrolytes based on cubically stabilized zirconia or perovskite-like LaGaO$_3$ [11]. The conductivity level is also higher than the value of 0.14 S/cm found in the ferrite Sr$_{0.8}$La$_{0.2}$FeO$_{3-\delta}$ from permeation experiments at $10^{-3} < p_{O_2} < 0.21$ atm and 850°C [4] where the crystalline structure of Sr$_{0.8}$La$_{0.2}$FeO$_{3-\delta}$ is that of perovskite. One can suppose from this comparison that the ion conductivity of Sr$_{0.7}$La$_{0.3}$FeO$_{3-\delta}$ in the high-pressure range, where crystalline structure of the oxide is also perovskite like, may decrease also to nearly the same level of about 0.1 S/cm.

As a rough approximation, all oxygen ions may participate in the conduction while almost all oxygen vacancies are disordered and, thus, may equally be available as sites for oxygen ions to jump in the perovskite structure. Both factors contribute to the high level of the oxygen ion conductivity that is often observed in perovskites. In contrast, the oxygen vacancies existing in the brownmillerite-like phase are ordered (Fig. 2). Such ordering usually renders a much reduced level of the ion conductivity, for example, in Ca$_3$TiFe$_2$O$_8$ where oxygen conductivity does not exceed 0.01 S/cm at 950°C [12]. The case of the brownmillerite-like form of Sr$_{0.7}$La$_{0.3}$FeO$_{3-\delta}$ is peculiar because of the large size of the Sr^{2+} ion, which results in only small differences in the pseudo-cubic perovskite lattice parameters $a/\sqrt{2} \approx b/3 \approx c/\sqrt{2}$ [10]. It is possible therefore that some amount of oxygen ions in the iron–oxygen octahedra can leave their regular positions, thus forming oxygen vacancies in the octahedra, and fill structural vacancies, thus forming interstitial oxygen ions, in the layers of iron–oxygen tetrahedra. This anti-Frenkel disordering reaction may be presented as

$$V_{O,\,tet} + O_{oct}^{2-} = O_{tet}^{2-} + V_{O,\,oct}, \qquad (2)$$
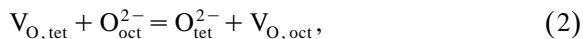
where V$_{O,\,tet}$ and V$_{O,\,oct}$ denote vacant oxygen positions in layers of the iron–oxygen tetrahedra and octahedra, respectively. Hence, two pathways for oxygen migration may be envisioned. The first is related to movement of the interstitial oxygen over structural vacancies that form one-dimensional tunnels in the layers of tetrahedra, whereas the second involves oxygen ion jumps over a two-dimensional network of vacancies in the layers of octahedra. The activation energy for ion jumps in the iron–oxygen

tetrahedra layers can generally be smaller than for the jumps over vacancies in the octahedra. However, the product of the redistributed oxygen concentration by the vacancy concentration, which defines the jump availability, is larger in the layers of octahedra than the respective value in the layers of tetrahedra. Therefore, the layers of the iron–oxygen octahedra, that is, the perovskite-like structural slabs, appear to provide a more viable pathway for the oxygen migration in the brownmillerite-like modification of the ferrite.

The evaluated oxygen ion conductivity and data for the total conductivity in Fig. 1 can be utilized together for plotting isotherms of the ion transference numbers in Sr$_{0.7}$La$_{0.3}$FeO$_{3-\delta}$. The ion conductivity level at $p_{O_2} > 10^{-4}$ atm is accepted to be equal to that in the range of smaller p_{O_2}, for example, 0.25 S/cm at 900°C, though this value is most possibly smaller in the high-pressure limit as pointed out above. Therefore, respective parts of the isotherms are drawn with dashed lines, which represent upper estimated levels for the transference numbers (Fig. 6). This figure illustrates quite directly that the mixed metal oxide Sr$_{0.7}$La$_{0.3}$FeO$_{3-\delta}$ is an attractive material for the design of an oxygen semipermeable membrane for the methane to syngas conversion process.

3.2. Electron–hole conductivity

The isothermal plots of the electron–hole conductivity, as obtained by subtraction of the ion conductivity from the total conductivity, are shown in Fig. 7. The slope of the conductivity isotherms is equal to $-1/4$ at p_{O_2} values left of the minima where thermopower is negative, whereas the slope is $+1/4$ and thermopower is positive at p_{O_2} values to the right of the minima. This behavior is characteristic of a nonstoichiometric semiconductor. The appearance of the conducting electrons in the ferrite may be explained by the loss of the lattice oxygen in the low-pressure limit

$$O^{2-} = 1/2O_2 + 2e^- \qquad K_n = [e^-]^2[O^{2-}]^{-1} p_{O_2}^{1/2}$$
$$= K_n^o \exp(-\Delta H_n / kT). \qquad (3)$$
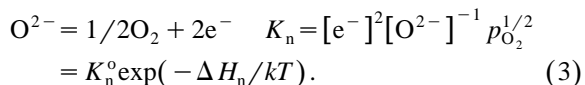
Here, K_n^o is a constant and ΔH_n is the reaction enthalpy. Supposing that the loss of oxygen is much smaller in comparison with the total amount of oxygen in the crystalline lattice, and neglecting the
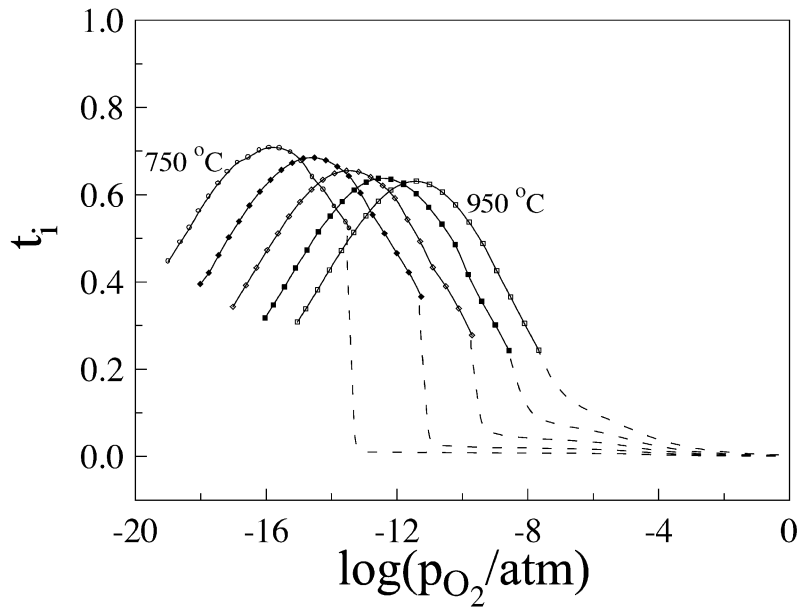
Fig. 6. The isothermal dependencies of the oxygen ion transference numbers versus the logarithm of oxygen partial pressure. The temperature interval between isotherms is 50°C. Data points correspond to values of A/σ. Solid lines serve as guides to the eyes. Dashed lines in the high-pressure range represent evaluated data.

mobility activation energy for electrons, the proportionality $\sigma_n \sim [e^-] \sim p_{O_2}^{-1/4}$ consistent with the experiment follows from the equilibrium constant. Also,

the conductivity activation energy for electrons must be about $\Delta H_n/2$. The respective value is found to be equal to 2.35 eV from the Arrhenius plot of $\sigma_n T$ at
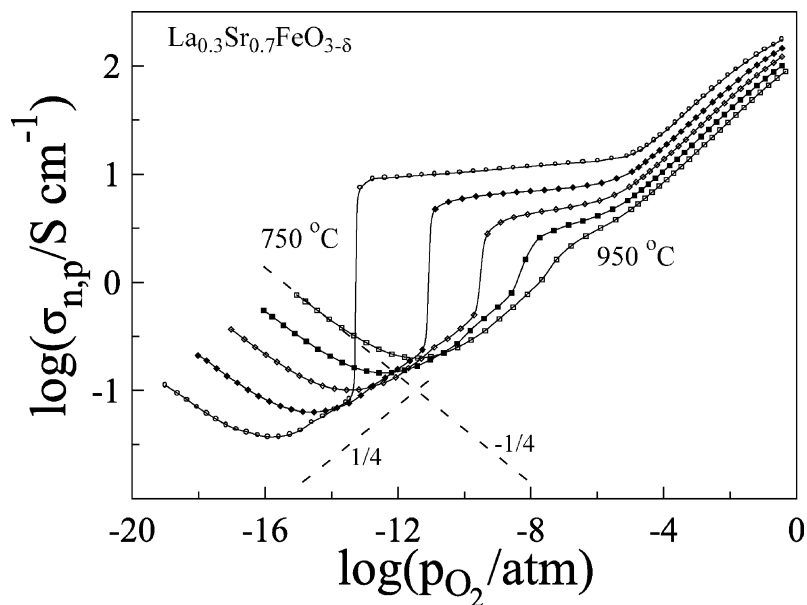

Fig. 7. The isothermal logarithmic plots of the electron–hole contribution in the conductivity depending on oxygen pressure. The temperature step between isotherms is 50°C.

$p_{O_2} = 10^{-16}$ atm (Fig. 5). Thus, neglecting the migration energy for electrons, the enthalpy ΔH_n may be estimated as equal to 4.7 eV. This value lies in line with the trend for the enthalpy to decrease with lanthanum content in $Sr_{1-x}La_xFeO_{3-\delta}$ as demonstrated in Refs. [1,2] where it was found that ΔH_n decreases from 7 eV at $x = 1$ to 4.5 eV at $x = 0.75$. The hole contribution increasing with the pressure to the right of the minima symmetrically with the increase of the electron contribution with the pressure decrease to the left of the minima in Fig. 7 is indicative of the internal equilibrium reaction

$$0 = e^- + h^+ \quad K_i = [e^-][h^+] = K_i^o\exp(-E_g/kT). \quad (4)$$

Here, K_i^o is a constant and E_g is a band gap. The parameter $C(T)$ in Table 1 is practically invariable with temperature and, thus, suggests a small activation energy both for the mobility and for the concentration of holes. On the other hand, combining equilibrium constants K_n and K_i, one can obtain

$$\sigma_p \sim [h^+] = \frac{K_i^o}{\left(K_n^o[O^{2-}]\right)^{1/2}}$$
$$\times \exp\left(-\frac{E_g - \Delta H_n/2}{kT}\right)p_{O_2}^{+1/4}. \quad (5)$$

This expression gives the correct slope for the conductivity isotherms to the right of the minima in Fig. 7. Moreover, we must conclude that the near equality $E_g - \Delta H_n/2 \approx -0.35$ eV is satisfied. Hence, the forbidden energy gap in the brownmillerite-like form of the ferrite $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ is equal to about 2.0 eV. It is close to values of E_g in $Sr_{1-x}La_xFeO_{3-\delta}$ given elsewhere for $0.75 \leq x \leq 0.9$ (2 eV) [1,2], $x = 0.4$ (1.9 eV) and $x = 0.2$ (1.7 eV) [3]. The band gap may alternatively be estimated from the temperature dependence of the minimal conductivity σ_{min} in Fig. 7. Expressing concentration of electrons and holes via σ_{min} and respective mobilities μ_n and μ_p, we can rearrange Eq. (4) in the form

$$K_i = K_i^o\exp(-E_g/kT) = \left[\sigma_{min}/2e(\mu_n\mu_p)^{1/2}\right]^2. \quad (6)$$

Assuming temperature-activated mobility for both electron- and hole-like carriers, $\mu_{n,p} = (\mu_{n,p}^o/T)\exp(-\varepsilon_{n,p}/kT)$, it follows from the plot of $\log(\sigma_{min}T)$ versus $1/T$ that $(E_g + \varepsilon_n + \varepsilon_p)/2 = 1.0$ eV (Fig. 5). As argued, the value ε_p of the hole mobility activation energy is nearly zero. Therefore, $(E_g + \varepsilon_n) = 2.0$ eV, which is equal exactly to the gap value given above if $\varepsilon_n \approx 0$. This derivation confirms the forbidden gap being equal to about 2.0 eV and additionally supports a small value of the mobility activation energy for electrons in $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ at a small oxygen pressure, that is, at large oxygen deficiency. Notice that the migration activation energy is also found close to zero both for electrons and holes in the lanthanum-rich $Sr_{1-x}La_xFeO_{3-\delta}$, where $0.75 \leq x \leq 1$ [1,2].

The results presented in this paper show that the concentration of electronic carriers in the low-pressure limit is governed by the band gap in the ferrite. The band gap may be expected when there are only trivalent iron ions in the oxide, that is, charge compensation is purely ionic. Therefore, the formula of the ferrite can be presented as $Sr_{0.7}La_{0.3}FeO_{2.65}$ at $p_{O_2}^{min}$ values corresponding to σ_{min} in Fig. 7. Changes in conductivity and thermopower isotherms in Fig. 7 show that variations of oxygen content in the oxide $Sr_{0.7}La_{0.3}FeO_{2.65}$ caused by moderate increase/decrease in the pressure are so small that the amount of additional holes/electrons appearing in the oxide in response to the oxygen intake/release is much smaller than the amount of holes/electrons existing in the oxide owing to the thermal excitation according to reaction (4). The appearance of nearly flat portions on the plots of conductivity and thermopower at a more pronounced increase in the pressure suggests that the conductivity acquires an impurity-controlled character, that is, becomes governed by the amount of the extra-stoichiometric oxygen δ in $Sr_{0.7}La_{0.3}FeO_{2.65+\delta}$. In other words, we suppose that the impurity-like band of acceptor states appears above the top of the valence band upon incorporation of some small, but critical amount of the extra-stoichiometric oxygen in the brownmillerite-like phase. The simultaneous transition of the oxide from semiconductor- to metal-like behavior may be interpreted as related to the shift of the Fermi level from a mid-gap position to the array of impurity-like states. It is important to notice that the pressure

increase, that is, the increase of the oxygen content in the oxide, finally results in the transition from brownmillerite-like to perovskite phase and in a simultaneous and smooth increase of the conductivity. Such an evolution may possibly be related not to the structural transition only but to the broadening of the impurity band also and its overlap with the states at the top of the valence band with a progressive incorporation of oxygen in the structure.

4. Conclusion

The electrical conductivity and thermopower were measured in the strontium ferrite $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ in the temperature range 750–950°C and oxygen pressure varying between 10^{-19} and 0.5 atm. Decreasing oxygen pressure results in the transition of the perovskite-like structure into brownmillerite-like structure $Sr_{0.7}La_{0.3}FeO_{2.65+\delta}$ below about 10^{-4} atm. The electron–hole conductivity in the brownmillerite-like phase is shown to be governed by the band gap of about 2.0 eV. The increasing extra-stoichiometry in $Sr_{0.7}La_{0.3}FeO_{2.65+\delta}$ results in appearance of acceptor states above the top of the valence band and transition of the conductivity to the impurity-controlled regime. The brownmillerite-like form of the ferrite is shown to be a mixed conductor with the oxygen conductivity level achieving about 0.3 S/cm at about 900°C and $p_{O_2} \approx 10^{-19}$ atm. It is argued that oxygen conduction takes place mainly in the perovskite-like layers of the structure.

References

[1] J. Mizusaki, T. Sasamo, W.R. Cannon, H.K. Bowen, J. Am. Ceram. Soc. 65 (1982) 363.
[2] J. Mizusaki, T. Sasamo, W.R. Cannon, H.K. Bowen, J. Am. Ceram. Soc. 66 (1983) 247.
[3] M.C. Kim, S.J. Park, H. Haneda, J. Tanaka, S. Shirasaki, Solid State Ionics 40/41 (1990) 239.
[4] Y. Teraoka, H.-M. Zhang, S. Furukawa, N. Yamazoe, Chem. Lett. (1985) 1743.
[5] Y. Teraoka, T. Nobunaga, K. Okamoto, N. Miura, N. Yamazoe, Solid State Ionics 48 (1991) 207.
[6] J.E. ten Elshof, H.J.M. Bouwmeester, H. Verweij, Solid State Ionics 81 (1995) 97.
[7] J.E. ten Elshof, H.J.M. Bouwmeester, H. Verweij, Solid State Ionics 89 (1996) 81.
[8] V.L. Kozhevnikov, I.A. Leonidov, M.V. Patrakeev, E.B. Mitberg, K.R. Poeppelmeier, J. Solid State Chem. 158 (2000) 320.
[9] N. Cusak, P. Kendall, Proc. Phys. Soc. 72 (1958) 898.
[10] P.D. Battle, T.C. Gibb, P. Lightfoot, J. Solid State Chem. 84 (1990) 237.
[11] T. Ishihara, H. Matsuda, M. Azmi bin Bustam, Y. Takita, Solid State Ionics 86–88 (1996) 197.
[12] M.V. Patrakeev, E.B. Mitberg, I.A. Leonidov, V.L. Kozhevnikov, unpublished data.