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p-Type electron transport in $La_{1-x}Sr_xFeO_{3-\delta}$ at high temperatures

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Abstract

Electrical conductivity, thermopower and oxygen content were measured for $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0.2$, 0.5, 0.9) within the oxygen partial pressure range 10^{-4}–0.5 atm and at temperatures 750–950 °C. The dominating charge carriers under these experimental conditions are electron holes. The results of oxygen nonstoichiometry measurements are used to estimate the concentration of holes and to analyze data on conductivity and thermopower. The changes in thermopower are described by the model assuming that the number of sites accessible for migration of holes is independent on oxygen content. The mobility of electron holes is calculated, and it is found to be virtually independent on temperature in the compositions with $x < 0.5$ while compositions with $x > 0.5$ exhibit thermally activated mobility and mobility values about $0.1 \, cm^2 \, V^{-1} \, s^{-1}$ or smaller. It is suggested that the main contribution to the composition dependent variations in electron hole mobility are associated with Coulomb interactions at small x's, whereas at high degrees of doping the mobility of holes is most strongly affected by the increasing amount of oxygen vacancies.
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1. Introduction

Lanthanum–strontium ferrites $La_{1-x}Sr_xFeO_{3-\delta}$ are good electron conductors. Moreover, these oxides exhibit a high level of oxygen-ion conductivity owing to the considerable concentration of vacancies on the anion sublattice. The increased interest in these oxides as electrode materials and oxygen semi-permeable membranes has led to intensive studies of the defect structure [1–4], thermodynamics [3–5], ion [6–9] and electron transport [1,2,10]. Under oxidizing conditions the predominant charge carriers in the ferrites are electron holes, and the concentration of these holes is strongly influenced by temperature and partial oxygen pressure in the gas phase. The features of the high-temperature electron hole transport at $p(O_2) > 10^{-4}$ atm in the ferrites with $x = 0$, 0.1, 0.25 were considered in works [1,2]

based on the charge carrier concentration derived from thermopower data under the assumption that all iron ions are accessible for migration of holes. However, this model may not always be correct because defect clusters and vacancy associates, which are known to persist in complex oxides even at high temperatures, can serve as charge traps thus decreasing the number of iron sites available for the transport. It was shown earlier [11,12] that at high strontium content some iron ions in $La_{1-x}Sr_xFeO_{3-\delta}$ indeed are excluded from the electron transfer. An alternative and more straightforward method to determine the concentration of hole carriers is to consider the oxygen nonstoichiometry and to analyze the dependence of the thermopower on the oxygen content in order to verify whether all the iron ions are actually involved in electron hole transport. Additional understanding of the transport features can be gained from the oxygen content dependent behavior of electric properties. In contrast to the low oxygen pressure/high oxygen deficiency limit [13,14], the present

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work analyzes the electron transport parameters of $La_{1-x}Sr_xFeO_{3-\delta}$ under oxidizing conditions in a wide range of strontium concentrations.

2. Experimental

The perovskite-type oxides $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0.2$, 0.5, 0.9) were prepared by a standard ceramic technique in air as described elsewhere [13,14]. The synthesized samples were ball-milled in ethanol media to a typical grain size of about 1 µm and pressed into disks under 2 kbar of uniaxial load. The discs were sintered in air at 1300–1350 °C to a density no less than 90% of theoretical. Rectangular bars $2 \times 2 \times 15$ mm^3 were cut from the sintered ceramic discs for electrical measurements. The electrical four-probe DC conductivity and thermopower were measured simultaneously as functions of oxygen pressure and temperature with the help of an electrochemical cell made of the cubically stabilized zirconia (YSZ). The cell was equipped with two pairs of Pt electrodes, which served as an oxygen pump and a sensor, thus enabling to change and to control oxygen partial pressure over the samples. The sample for thermopower measurements was placed along natural temperature gradient in the cell (about 15 °C/cm). Two S-type thermocouples were attached to the butt ends of the sample after sheets of Pt foil; the Pt leads of the thermocouples served also as thermovoltage probes. The measured results were corrected for the contribution of platinum [15]. The second sample, which served for measurements of conductivity, was placed in the experimental cell in a crosswise orientation near the middle of the sample for Seebeck coefficient measurements, i.e. in an isothermal plane of the cell. The voltage and current probes were made of Pt wire ($\varnothing 0.3$ mm) and tightly wound to the bar at about 8 mm and 14 mm, respectively. The configuration of the probes was symmetrical relative to the center of the sample. The electrical parameters of the experiments were measured using a high-precise voltmeter Solartron 7081. The experimental procedures for oxygen pressure variations inside the cell and the sample equilibration control were described elsewhere [16]. The criterion for equilibration of a sample after a change in either oxygen pressure or temperature included the relaxation rates of the conductivity and Seebeck coefficient less than 0.01% min^{-1} and 0.001 µV K^{-1} min^{-1}, respectively. Measurements were performed in the oxygen pressure interval 10^{-4}–0.5 atm and at temperatures within 750–950 °C. The oxygen content variations in the ferrites were measured depending on oxygen partial pressure and temperature by means of the coulometric titration technique in a double cell. Measurements were carried out in the same limits of oxygen pressure and temperature as for electrical tests. The powdered

samples were employed for the measurements in order to accelerate oxygen exchange and diffusion processes. The experimental procedure is described elsewhere in more details [17]. The absolute values of the oxygen content in as-prepared samples were determined by reduction in a Setaram TG-DTA-92 thermoanalyzer using a 5%H$_2$:95%He gas mixture. These data and results for $x = 0.7$ and 1.0 from previous work [11,12] were combined in this study.

3. Results and discussion

The results of electrical conductivity and thermopower measurements in $La_{1-x}Sr_xFeO_{3-\delta}$ ($x = 0.2$, 0.5, 0.9) at different temperatures and partial oxygen pressures are given in Figs. 1 and 2. The positive sign of thermopower and decrease in the conductivity at reduction of oxygen partial pressure both show that the dominating charge carriers under these particular experimental conditions are electron holes.
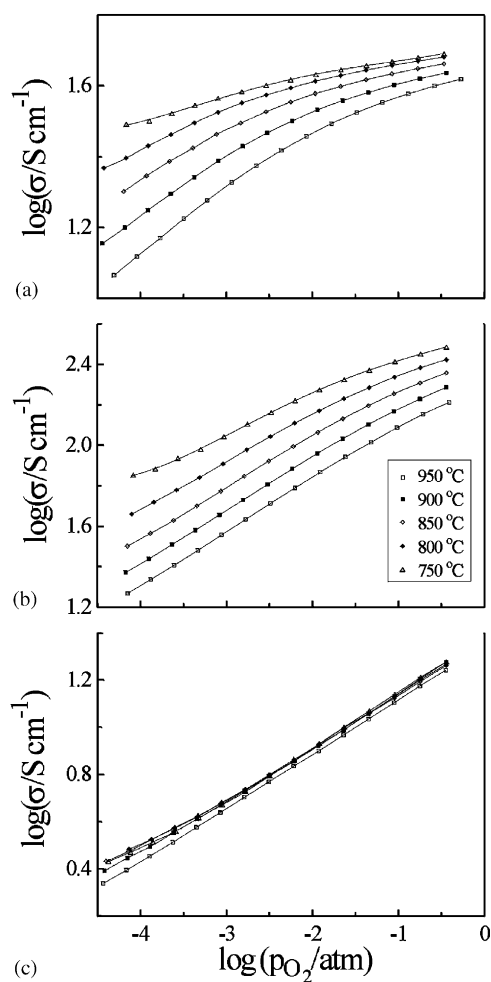

Fig. 1. Electrical conductivity vs. partial pressure of oxygen for $La_{1-x}Sr_xFeO_{3-\delta}$. (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.9$. Solid lines serve as a guide to the eye.

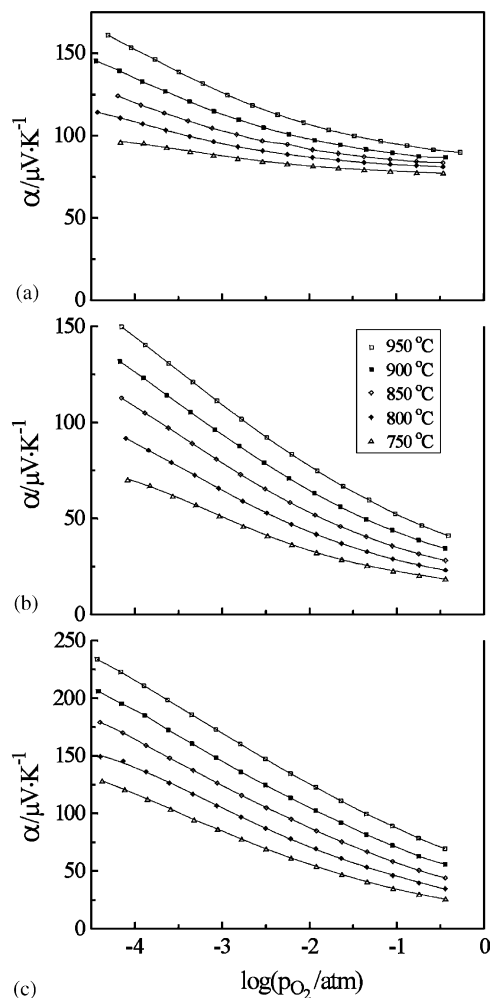Fig. 2. Thermopower vs. partial pressure of oxygen for La$_{1-x}$Sr$_x$FeO$_{3-\delta}$. (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.9$. Solid lines serve as a guide to the eye.

Ion conductivity in these ferrites is small in comparison with the overall conductivity in the pressure interval $p(O_2) = 10^{-4}$–0.5 atm [13,14]. For example, at $p(O_2) = 10^{-4}$ atm the ion contribution does not exceed 1%, 3% and 5% of the overall conductivity for the compositions with $x = 0.2$, 0.5 and 0.9, respectively. Therefore the experimental values of the electrical conductivity can be considered equal to the hole conductivity σ_p with good precision. The conductivity increases with the change in strontium content from $x = 0.2$ to 0.5, while σ_p decreases as x increases further to 0.9, Fig. 1. These variations in the conductivity have their origin in changes in both the concentration and mobility of the charge carriers. The relatively large values of thermopower under high pressures for the composition with $x = 0.2$ reflect the lower concentration of holes in this oxide at this composition compared to the compositions with $x = 0.5$ and 0.9. Because a variation in temperature leads to changes in oxygen content, it is desirable to know the oxygen content for

each value of x as a function of the temperature and oxygen pressure in equilibrium with the gas phase in order to perform further analysis of electron transport. The oxygen nonstoichiometry (δ) in the La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ ferrites was measured earlier for the compositions with $x = 0$, 0.1, 0.25, 0.4 and 0.6 [3,4]. In this study similar data on the oxygen content ($3-\delta$) in the examined oxides La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ ($x = 0.2$, 0.5, 0.9) were found as shown in Fig. 3 at different values of temperature and oxygen partial pressure. The wide oxygen homogeneity range, which is observed in these ferrites, is a characteristic feature of complex oxides with a perovskite structure containing variable-valence *B*-cations in different oxidation states. The partial replacement of trivalent lanthanum for divalent strontium results in decreased stability of the crystal lattice on heating, and rather intensive formation of oxygen vacancies competes with the oxidation of the iron. In order to discuss the possible responses of an oxide system two extremes need to be considered on introduction of the dopants (Sr^{2+}). Ionic compensation of acceptors and the formation of oxygen vacancies occur when the oxidation state of the iron cations remains unchanged ($+3$). Electronic compensation involves only a change of the oxidation state of iron cations from $+3$ to $+4$, which may be interpreted as an appearance of electron holes associated with Fe^{4+} cations. Both types of charge compensation in the La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ ferrites can proceed simultaneously [2,4] and the contribution of each mechanism to the formation of charge carriers depends on acceptor concentration, temperature and partial oxygen pressure. The concentration of Fe^{4+} ions can be considered as a quantitative characteristic of the equilibrium where formation of oxygen vacancies and changes in the oxidation state of iron cations are bound by conditions of electrical neutrality and lattice conservation so that the following relationship is fulfilled for the ferrite of the general formula La$^{3+}_{1-x}$Sr$^{2+}_x$Fe$^{3+}_{1-\gamma}$Fe$^{4+}_\gamma$O$^{2-}_{3-\delta}$

$$\gamma = [Fe^{4+}] = [h^+] = x - 2\delta. \qquad (1)$$

The experimental data in Figs. 1–3 and results from earlier studies [11,12] were utilized to plot Fig. 4. At small levels of doping the concentration of hole carriers increases nearly linearly with strontium content (see Fig. 4(a)) thus indicating mostly electronic compensation of acceptors in the high-pressure limit of the experimental data. The increase in doping and temperature both result in the decrease of the amount of holes, which reflects an increase in ionic compensation.

Electron transport in ferrites occurs via the Fe^{4+}–O^{2-}–Fe^{3+} chains. Therefore, all species entering the chains influence the total conductivity. This observation is supported by the isothermal dependences of conductivity as a function of strontium content
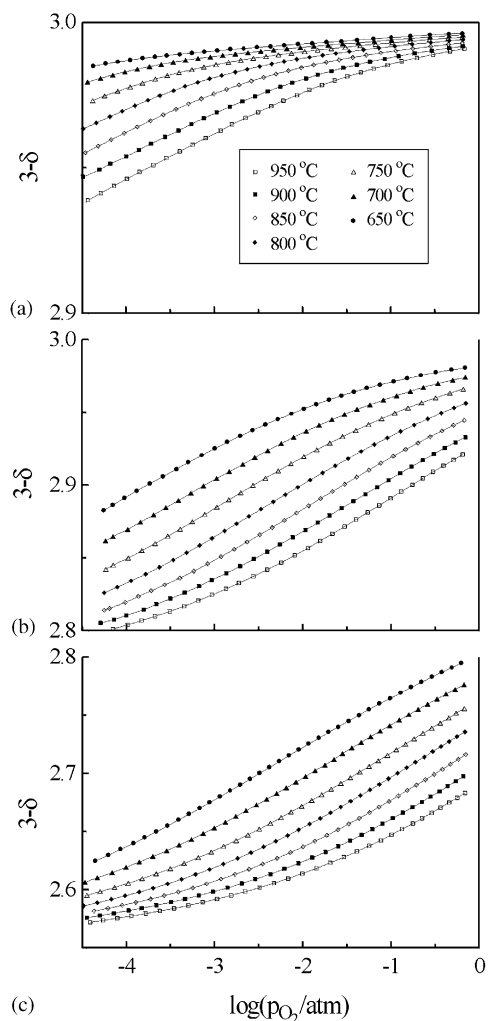
Fig. 3. Oxygen content vs. partial pressure of oxygen for $La_{1-x}Sr_xFeO_{3-\delta}$. (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.9$. Solid lines serve as a guide to the eye.

Fig. 4. The concentration of electron holes per formula unit (a) and conductivity (b) as functions of strontium content in $La_{1-x}Sr_xFeO_{3-\delta}$ at $p(O_2) = 0.5$ atm. Solid lines serve as a guide to the eye.

(see Fig. 4(b)), which exhibit a more complicated behavior compared to the $\gamma(x)$ curves in Fig. 4(a). The concentration of Fe^{3+} ions participating in electron transport may be estimated from thermopower. Fig. 5 presents isothermal dependences of thermopower and conductivity vs. oxygen content in $La_{1-x}Sr_xFeO_{3-\delta}$, as well as the corresponding data for the compositions with $x = 0.7$ and 1 published earlier [11,12]. The temperature dependence of the isotherms is rather weak and the main changes in conductivity and thermopower are brought about by variations in the oxygen content. The non-linear, almost parabolic shape of the conductivity isotherms suggests that not only the concentration of charge carriers, but also their mobility increases with the content of oxygen. Assuming a jump-like movement of hole carriers and neglecting the heat of transport, the following well-known expression [18] may be used to analyze the thermopower:
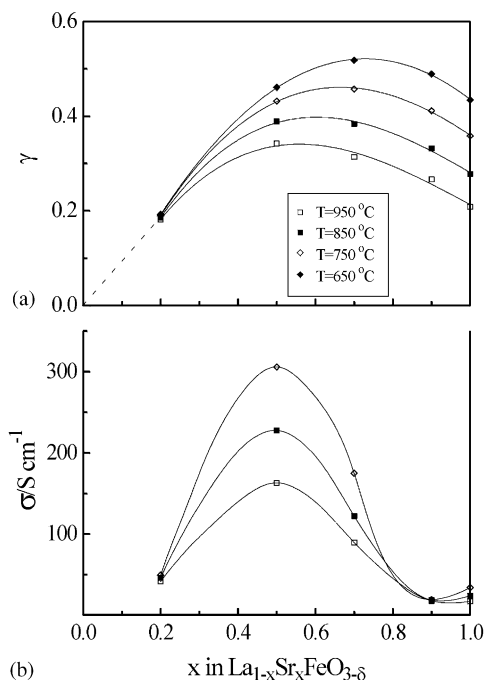
$$\alpha = \frac{k}{e}\ln\left(\frac{1}{\beta}\frac{N_p}{p}\right). \tag{2}$$

Here, k and e are Boltzmann constant and the absolute value of the elementary charge, respectively, p is the number of electron holes (Fe^{4+}), N_p is the number of positions (Fe^{3+}) available for hole jumps. The degeneracy factor is expressed by $\beta = (2S_3 + 1)/(2S_4 + 1)$, where S_3 and S_4 denote the spin numbers for Fe^{3+} and Fe^{4+}, respectively. Literature data [19] indicate that at elevated temperatures iron ions in the perovskite structure are characterized by a high-spin state ($S_3 = 5/2$ and $S_4 = 2$). For this reason in our subsequent calculations we used the value $\beta = 6/5$. The starting model for interpretation of the thermopower data was based on the supposition that electron holes located on Fe^{4+} ions may jump on any Fe^{3+} ions. In this case the number of accessible positions should be equal to unity at $\gamma = 0$ and $\delta = x/2$ and it should decrease as the concentration of oxygen increases since the incorporation of one oxygen ion in the crystal lattice gives rise to two holes. Taking into consideration this mechanism of variation in the number of carriers and accessible positions, expression (2) can be rewritten as

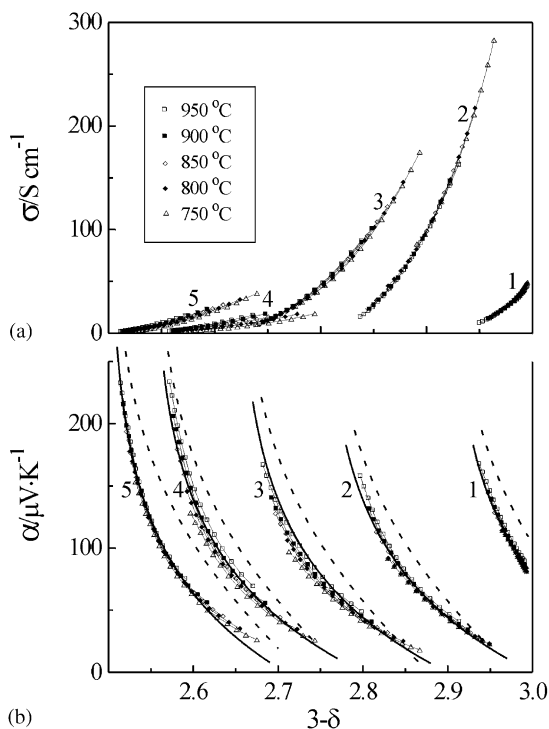$$\alpha = \frac{k}{e}\ln\left(\frac{1}{\beta}\frac{1 - (x - 2\delta)}{x - 2\delta}\right). \tag{3}$$

Fig. 5. Conductivity (a) and thermopower (b) in $La_{1-x}Sr_xFeO_{3-\delta}$ as functions of oxygen content. (1) $x = 0.2$, (2) $x = 0.5$, (3) $x = 0.7$ (data from [11]), (4) $x = 0.9$, (5) $x = 1$(data from [12]). The dashed lines in (b) show thermopower calculated according Eq. (3) while solid lines show calculated thermopower with $N_p = 0.5$.

The calculated variations of thermopower with oxygen content occur in accord with the observed trends at different strontium doping, while absolute values considerably exceed the experimental data, dashed lines in Fig. 5(b). The disagreement may be either because the actual amount of holes is smaller compared to $(x-2\delta)$ or because the number of available states $1-(x-2\delta)$ is overestimated in the model. There is no reason for the first assumption because it follows from the electrical neutrality requirement. Therefore, we assume that the number of accessible positions is smaller than is accepted in Eq. (3). Indeed, the jump of the hole from a Fe^{4+} cation to the neighboring Fe^{3+} cation likely does not occur when an oxygen vacancy separates the cations. Thus, the number of available states tends to be smaller than unity even in the limit of purely ionic compensation when $\delta = x/2$. On the other hand, in the limit of electronic compensation when an oxygen fills this vacancy, it transforms the Fe^{3+} to an Fe^{4+} cation and the respective hole jump again is prohibited. Hence, the number of available iron positions in the iron-oxygen network may be less sensitive to the hole content variations than is assumed in Eq. (3). With these arguments in mind we used the empirical expression $N_p = a - b(x - 2\delta)$ to fit the obtained data. Having considered several possible alternatives, we ascertained that a model with the amount of available positions
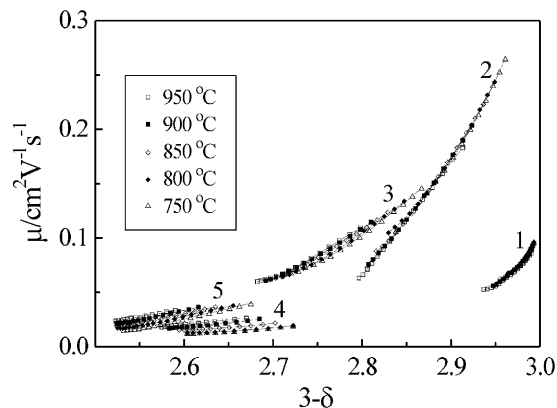

Fig. 6. Mobility of holes in $La_{1-x}Sr_xFeO_{3-\delta}$ as a function of oxygen content. (1) $x = 0.2$, (2) $x = 0.5$, (3) $x = 0.7$ (data from [11]), (4) $x = 0.9$, (5) $x = 1$ (data from [12]).

N_{const} invariably equal to about 0.5–0.6 enables a very good description of the experiment, solid lines in Fig. 5(b). Further work is necessary to better understand the mechanism underlying formation of the effective density of available states in these ferrites.

The electrical conductivity is proportional to the product of the charge carrier concentration by the concentration of accessible positions. Since N_{const} is practically a constant, the respective product should follow the shape of the $\gamma(x)$ curves. However, it can be seen in Fig. 4 that the σ_p vs. x differs from the γ vs. x dependence. We can conclude, therefore, that mobility changes with composition appreciably affect the overall dependence of conductivity in $La_{1-x}Sr_xFeO_{3-\delta}$. The mobility of charge carriers can be calculated as $\mu = \sigma/(Ne\gamma)$, where N is the number of unit cells per $1\,cm^3$ calculated from structural data [13]. These results are shown in Fig. 6. It is seen from this plot that the mobility of holes indeed increases with the content of oxygen in the lattice. An increase in strontium concentration from $x = 0.2$ to 0.5 results in an increase of hole mobility at fixed temperature, while further increase in the dopant content reduces the mobility of carriers, see Fig. 7. The mobility increase caused by substitution of lanthanum for strontium can be explained as resulting from variations in Coulomb interactions along the migration pathway of electron holes (Fe^{4+}–O^{2-}–Fe^{3+}). Clearly, it is more difficult for the hole to overcome Coulomb repulsions induced by La^{3+} ions around the oxygen anion in the chain Fe^{4+}–O^{2-}–Fe^{3+} than the barrier created by Sr^{2+} ions having smaller charge. The defectiveness of the anion sub-lattice appreciably increases with further increase in strontium content. For instance, it is seen from Fig. 8 that for about ten electron holes there is approximately one oxygen vacancy at $x = 0.5$ whereas the number of holes and vacancies become comparable at $x = 0.9$. Thus, multiple vacancies not only disrupt conducting chains
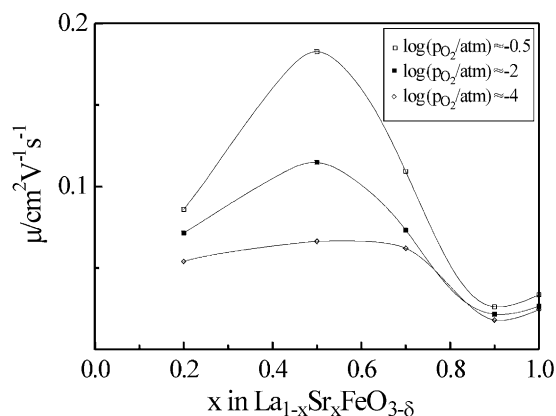
Fig. 7. Mobility of holes in $La_{1-x}Sr_xFeO_{3-\delta}$ as a function of strontium content at 950 °C. Solid lines serve as a guide to the eye.
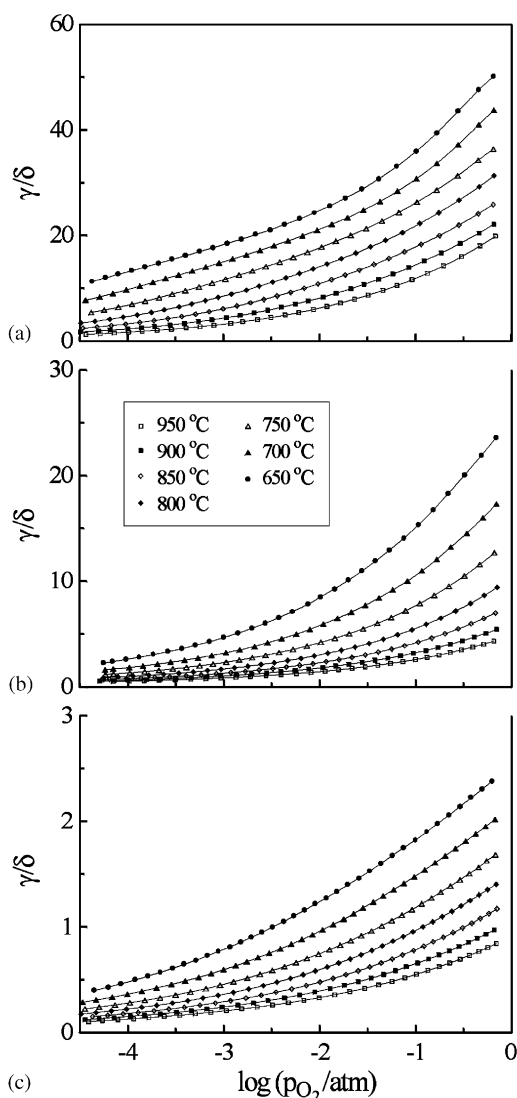

Fig. 8. The ratio of the concentration of holes to the concentration of oxygen vacancies in $La_{1-x}Sr_xFeO_{3-\delta}$ as a function of partial oxygen pressure. (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.9$. Solid lines serve as a guide to the eye.

$Fe^{4+}-O^{2-}-Fe^{3+}$ but also result in substantial local deformations of the remaining migration pathways thus decreasing the mobility for values of $x > 0.5$. The high level of anion defects is the reason also for the increase in the migration activation energy. Simple estimates reveal the mobility activation energy about ~0.4 and ~0.2 eV in the oxides with $x = 1.0$ and 0.7, respectively, while it tends to nearly zero values at $x \leqslant 0.5$. One last remark can be made concerning the mobility being somewhat larger in $SrFeO_{3-\delta}$ than in $La_{0.1}Sr_{0.9}FeO_{3-\delta}$ though it may be expected to be nearly the same or at a smaller value considering changes in the interval $0.5 \leqslant x \leqslant 0.9$. This variation can possibly occur because it is relatively easier for the hole to overcome the symmetrical Coulomb barrier formed by the field of Sr^{2+} cations compared to a more random barrier owing to introduction of lanthanum in place of strontium.

On the whole, the thermally activated behavior of hole mobility and its values in the oxides with $x > 0.5$ correspond to a high-temperature conduction mechanism provided by jumps of small polarons. The disordering of the crystal lattice aroused by oxygen vacancies and dopant additives seem to be the major reason for the localized character of electron hole carriers in $La_{1-x}Sr_xFeO_{3-\delta}$. The mobility in ferrites having $x < 0.5$ acquires nonactivated character though changes with oxygen content and absolute values of thermopower are quite similar to those at $x > 0.5$. The border between the two regimes of conduction is marked with highest mobility of holes, an effect which seems to arise from the interplay of Coulomb interactions with the A-cations and the random probability of oxygen vacancies along the migration pathway.

Acknowledgments

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