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## Influence of A-site deficiencies in the system $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ on structure and electrical conductivity

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**Abstract** In this study, the A-site-deficient  $\text{ABO}_3$  perovskites  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  with  $x = 0.025, 0.05, 0.075, 0.1, \text{ and } 0.2$  were prepared by conventional solid state reactions. X-ray investigations were carried out in order to determine the influence of the A-site deficiencies on the structure. The electrical conductivities were measured as a function of both temperature and oxygen partial pressure in ranges 500–1000 °C and  $0.2\text{--}10^{-6}$  atm, respectively. Only for small  $x$  values were single phases obtained. All compositions with A-site deficiencies exhibit a lower conductivity compared to the stoichiometric compound. It is shown by SEM micrographs that the sample morphology is changed by an A-site-deficient preparation as well. For A-site-deficient compositions, a reduction of the grain size is observed, most likely due to impurity inclusions in the grain boundaries.

**Keywords** LSGM perovskite · Oxide ion conductor · Perovskite · Solid electrolyte · Solid oxide fuel cells

### Introduction

Solid oxide fuel cells (SOFCs) based on yttrium stabilized zirconia (YSZ) as a solid electrolyte material offer a good opportunity for decentralized heat and energy

supply. A problem is the high operating temperature of SOFCs, typically around 900–1000 °C, which is necessary for the YSZ electrolyte to have sufficiently high oxide ion conductivity. The main problems caused by the high operating temperature are: the material's stability and compatibility, thermal degradation, and the high costs of periphery materials. An operating temperature below 800 °C would have major advantages concerning the lifetime of the stack and costs. In order to decrease the operating temperature, new solid electrolytes with high oxide ion conduction of more than  $10^{-2}$  S/cm at temperatures below 800 °C are required.

Perovskites offer an interesting alternative to the fluorite-based YSZ material. Doping with cations of lower valences can create oxygen vacancies in the perovskite structure, which is of high importance for oxide ion conduction. For instance, in the  $\text{LaGaO}_3$  system, the substitution of the A-site  $\text{La}^{3+}$  by  $\text{Sr}^{2+}$  and the B-site  $\text{Ga}^{3+}$  by  $\text{Mg}^{2+}$  is followed by the formation of oxygen vacancies. The  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  (LSGM) perovskite, which was investigated by Ishihara et al. [1, 2] and Huang and Petric [3], exhibits a higher ionic conductivity than YSZ at the same temperatures. Another advantage of perovskite solid electrolytes is that their structure is similar to other perovskite materials which are used for electrodes and interconnections. It is hoped that new combinations of electrolyte, electrode, and interconnection materials, with smaller differences in thermal expansion coefficients and higher adhesion, would improve the long-term stability and reduce the segregation, solution, and enrichment of the components.

However, there are also some disadvantages of the LSGM material concerning its use as a solid electrolyte. Lanthanum-containing materials are sensitive to water vapor and carbon dioxide, if traces of oxides are present. Furthermore, a small oxygen partial pressure dependence of the electrical conductivity exists, particularly at high oxygen partial pressures. All in all, it is necessary to improve the properties of the LSGM perovskite [8, 9, 10, 11, 12, 13, 14, 15].

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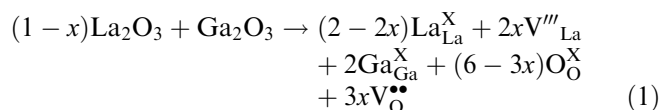
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First, there is the possibility of complete cation substitution. The A-cation,  $\text{La}^{3+}$ , can be completely replaced by only a few ions, e.g.  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , but no improvement of the oxide ion conductivity is obtained [4]. A complete substitution of  $\text{La}^{3+}$  by other rare earth ions, e.g.  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$ , leads to the formation of garnets in most cases. The garnet structure is unsuitable for oxide ion conduction. The corner-sharing octahedra and tetrahedra are twisted toward each other and it is unlikely that oxide ion conduction can occur [5].

Another possibility to change the electrical and electrocatalytic properties of perovskite materials is the introduction of defects and vacancies into the structure. The perovskite structure is able to accommodate a wide range of cations with different sizes and valences at both the A- and B-sites. It also tolerates deviations from exact stoichiometry, especially cation and oxygen deficiency. In A-site-deficient perovskites which are based on metals in mixed valence states, e.g. chromites and manganites, the charge compensation for the formation of A-site vacancies leads to a change in oxidation state of the B-cations, e.g.  $\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$  [6] and  $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$ , or to the formation of additional oxygen vacancies and therefore to an increase in electrical conductivity. These materials are well-known mixed conductors.

In order to develop stable perovskite materials with a high concentration of oxygen vacancies and high oxide ion conductivity, we are looking for systems with B-site cations in fixed oxidation states. In this case the charge compensation mechanism should take place according to Eq. 1, which represents the formation of oxygen vacancies in an A-site-deficient  $\text{LaGaO}_3$  perovskite:



This possible creation of oxygen vacancies by incorporation of A-site vacancies increases the concentration of charge carriers and might improve the electrical properties of the material. This is the main purpose for our investigation of A-site-deficient LSGM materials. Furthermore, a slightly deficient  $\text{La}^{3+}$  substoichiometry in the perovskite lattice should prevent the formation of  $\text{La}_2\text{O}_3$ , which hydrates rapidly and forms hydroxides responsible for deterioration of the mechanical strength. Therefore, better long-term stability is expected for A-site-deficient LSGM materials.

## Experimental

Stoichiometric  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ , related to the Ishihara compound, and new non-stoichiometric compositions  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  with  $x=0.025, 0.05, 0.075, 0.1,$  and  $0.2$  were prepared. The powders were prepared by conventional solid state reaction. The starting materials [ $\text{La}_2\text{O}_3$  (Merck),  $\text{Ga}_2\text{O}_3$ ,  $\text{SrCO}_3$  (99.99%, Aldrich), and  $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (99%, Aldrich)] were weighed out in required proportions and mixed together. Calcination was carried out at  $1150^\circ\text{C}$ . The product was reground and finally sintered at  $1500^\circ\text{C}$  in air for 12 h.

The crystal structures of the products were characterized by X-ray powder diffraction using a Siemens D-5000 transmission diffractometer and Cu-K $\alpha$  radiation. For conductivity measurements, the powders were pressed into pellets of 8 mm diameter and 2–3 mm thickness and again fired at  $1500^\circ\text{C}$ . The pellets were coated with platinum paste on both sides and then sintered at  $1000^\circ\text{C}$ .

AC impedance measurements were carried out over the frequency range 0.1 Hz to 100 kHz, using an EG&G impedance/gain-phase analyzer. Data were collected as a function of both temperature and oxygen partial pressure in the range  $750\text{--}1000^\circ\text{C}$  and from 0.2 to about  $10^{-6}$  atm, respectively. The oxygen partial pressure was varied by using an electrolyzing cell based on YSZ.

## Results

### X-ray investigations and microstructure

Figure 1 shows X-ray patterns for the stoichiometric sample  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  and for the non-stoichiometric samples  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  with  $x=0.025, 0.05, 0.075, 0.1,$  and  $0.2$ . The patterns could be indexed by an orthorhombic unit cell, space group  $Pnma$ . All patterns, except the composition with  $x=0.2$ , were found without additional peaks of second phases. However, we have to take into account that there is a detection limit of ca. 3% and we are not able to detect minor phases at lower concentrations. We obtained additional peaks of a second phase with unknown composition for  $x=0.2$ , but the lower deficient samples probably contain some impurities not detectable by XRD. Other authors [10, 11, 12, 16] have obtained similar results; the LSGM perovskite structure tolerates only a very limited amount of A-site cationic deficiencies.

It was observed that with higher  $x$ -values, which represent a lower La content, the peaks are slightly shifted towards higher  $2\theta$  values. As listed in Table 1, the unit cell volume decreased from  $239.4 \text{ \AA}^3$  for the stoichiometric sample with  $x=0$  to  $236.8 \text{ \AA}^3$  for the non-stoichiometric  $\text{La}_{0.875}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  ( $x=0.025$ ) material. The change in cell volume from  $x=0.025$  to

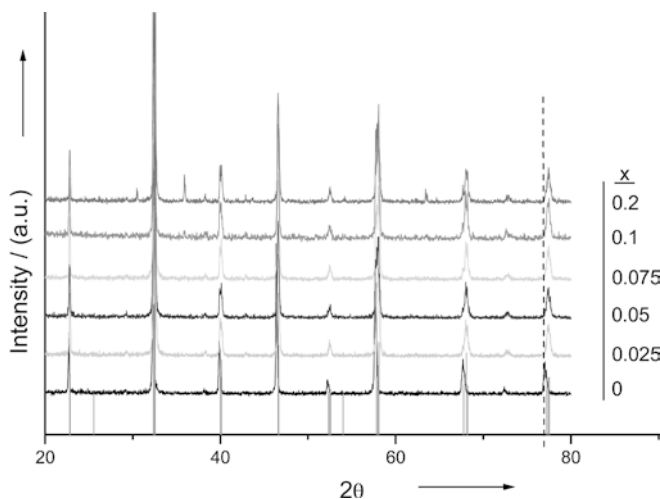


Fig. 1 X-ray diffraction patterns of  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$

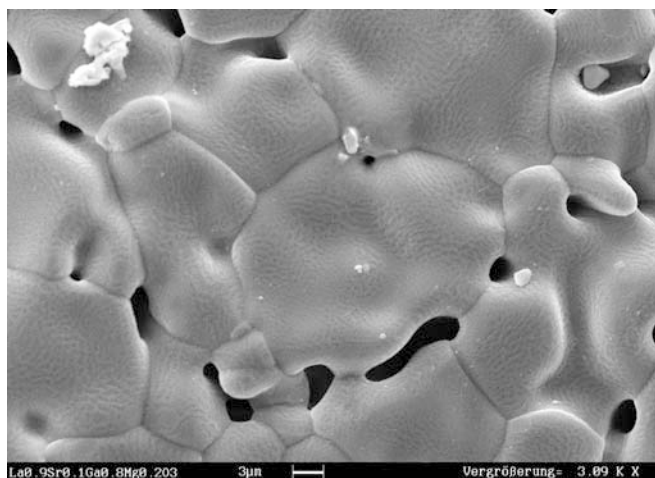
**Table 1** Calculated unit cell volumes

Compound	Cell volume, $V$ ( $\text{\AA}^3$ )
$\text{La}_{1.0}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	239.04
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	239.40
$\text{La}_{0.875}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	236.76
$\text{La}_{0.85}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	236.88
$\text{La}_{0.825}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	236.89
$\text{La}_{0.8}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	237.19
$\text{La}_{0.7}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	237.19

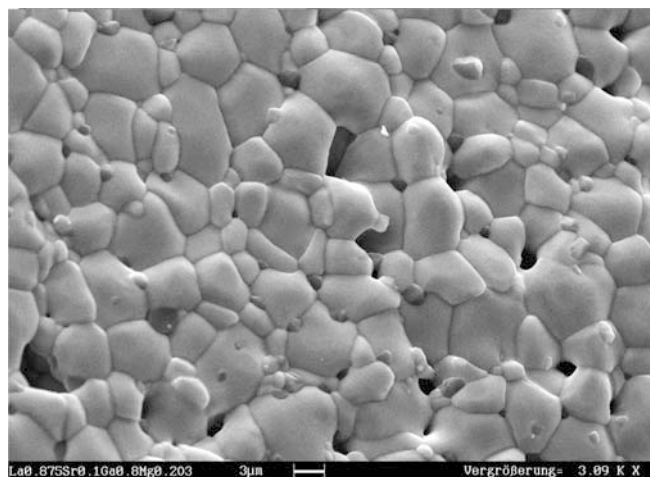
higher  $x$ -values increased very slightly. We believe that the decrease in cell volume is due to A-site cation deficiencies. On the other hand, oxygen vacancies created by A-site deficiencies should increase the cell volume. Hence we assume that both cation vacancies and oxygen vacancies are responsible for the change in cell volume at small  $x$ -values. However, at least at  $x$ -values higher than 0.025, minor amounts of second phases might be formed which cannot be detected by X-ray diffraction and the composition of the main phase does not refer to the overall material composition. SEM investigations confirmed the existence of secondary phases. It was shown by SEM micrographs that already a little substoichiometry in the A-sites prevents grain growth. The grain size of the non-stoichiometric material is much smaller than that of the stoichiometric one (Fig. 2 and Fig. 3). An explanation could be the presence of secondary phases in the grain boundaries, which prevent the growth of grains. Moreover, we observed some small spherical particles (most probably MgO [16]) by SEM (Fig. 3). Further investigations are necessary to indicate the tolerance limit for A-site vacancies in this perovskite system.

### Conductivity measurements

The objective of the conductivity measurements was to investigate how the compositional and structural chan-



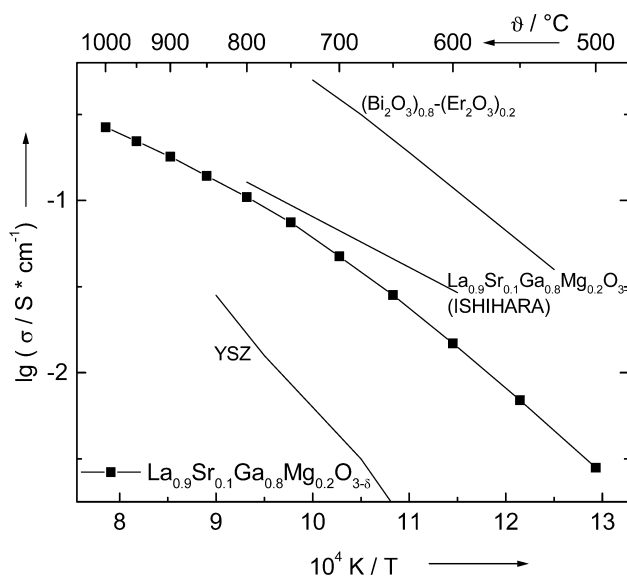
**Fig. 2** SEM micrograph of stoichiometric  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$



**Fig. 3** SEM micrograph of the A-site substoichiometric sample  $\text{La}_{0.875}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$

ges influence the electrical behavior of the non-stoichiometric materials. The conductivity was obtained by analyzing the complex impedance plots. The first intercept of the Nyquist plot semicircle with the  $x$ -axis (real part of the impedance) is related to the solid electrolyte resistance.

Figure 4 shows Arrhenius plots of the total conductivity values for the prepared stoichiometric sample  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  in comparison to the values given by Ishihara et al. [1] (fitted linearly over the temperature range) and other well-known electrolytes such as YSZ and  $\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_3$ . The  $\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_3$  material exhibits the highest conductivity but is not stable enough against reduction. The conductivity of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  is lower than  $\text{Bi}_{0.8}\text{Er}_{0.2}\text{O}_3$  but higher than that of YSZ. A deviation of the Arrhenius plot from linearity was obtained by Ishihara et al. as well as in our own studies. The investigated material exhibits



**Fig. 4** Arrhenius plot of  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$

slightly lower conductivity values than those reported by Ishihara et al. [1].

Figure 5 shows Arrhenius plots of the non-stoichiometric  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  ( $x=0-0.2$ ) samples in comparison with the data for the stoichiometric compound  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ . It was observed that the conductivity decreased with increasing  $x$ -values in the system  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ . As observed by other authors [12, 16], a non-stoichiometric preparation for the A/B ratio did not lead to improved electrical conductivity behavior. Several factors could cause the conductivity deterioration, especially the change of structural parameters, impurities, and/or defect clustering/ordering related to  $x$ -values and to the defect concentration, respectively. However, based on our X-ray results we have to assume that at  $x$ -values higher than 0.025 the impurity effect becomes more important. The activation energies determined from Arrhenius plots were fitted over two temperature ranges: from 750 °C up to 850 °C and from 900 °C up to 1000 °C. The calculated values obtained for the stoichiometric sample are higher than the activation energies determined for the non-stoichiometric samples. However, the activation energy for the non-stoichiometric samples increases with increasing  $x$ -values, most likely because the amount of impurities increased. Furthermore, we found two different temperature regions for the activation energy. Activation energy values calculated from the Arrhenius plots are listed in Table 2.

Conductivity measurements were also carried out isothermally in dependence on the oxygen partial pressure. It was reported by Ishihara et al. [1] that the conductivity of the stoichiometric LSGM is almost independent of the oxygen partial pressure below  $10^{-5}$  atm. Above this value, the electrical conductivity slightly increases with increasing partial pressures. Therefore, our measurements were carried out at oxygen

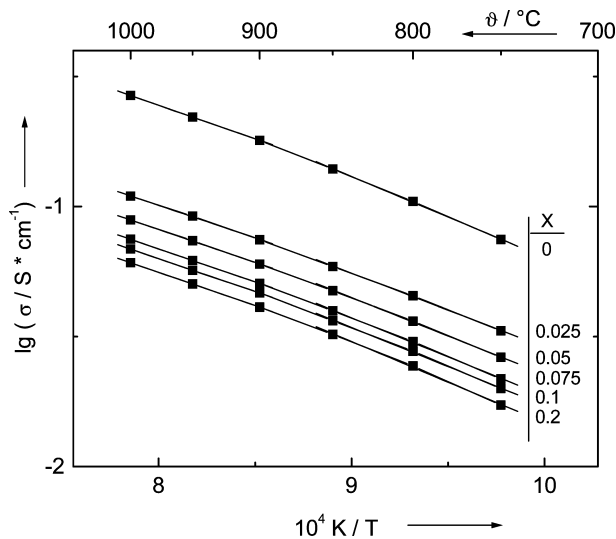
**Table 2** Activation energies of conductivity for the prepared materials

Compound	$E_a(1)$ (eV)	$E_a(2)$ (eV)
	750–850 °C	900–1000 °C
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.616	0.509
$\text{La}_{0.875}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.565	0.496
$\text{La}_{0.85}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.585	0.500
$\text{La}_{0.825}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.596	0.504
$\text{La}_{0.8}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.596	0.502
$\text{La}_{0.7}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$	0.618	0.508

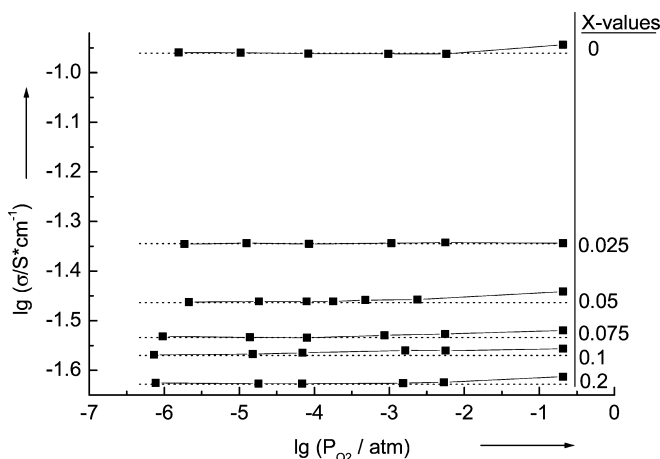
partial pressures ranging from 0.2 to  $10^{-6}$  atm. Figure 6 shows electrical conductivity values for the non-stoichiometric samples  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  for  $x=0, 0.025, 0.05, 0.075, 0.1, \text{ and } 0.2$ , obtained at 800 °C, in dependence on the oxygen partial pressure. In all cases, a small increase in conductivity was observed with increasing oxygen partial pressure, which indicates a small contribution of hole conduction at higher oxygen partial pressures. We also obtained that the conductivity dependence on the oxygen partial pressure becomes less significant at higher  $x$ -values. On the other hand, a wider range of conductivity dependence on oxygen partial pressure was observed with increasing  $x$ -values.

## Conclusions

The LSGM perovskite accepts only a small amount of A-site deficiencies. A limit for the solid solution or a tolerance limit for A-site vacancies exists between  $x=0$  and  $x=0.1$  in the  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  material. We found evidence that, at higher  $x$ -values, secondary phases form. Altogether, A-site deficiencies result in a small decrease in electrical conductivity in the investigated temperature range. Different parameters could be responsible for this. First of all, the decrease in unit cell volume is accompanied by changes of lattice parameters



**Fig. 5** Effect of non-stoichiometry on the conductivity of  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$



**Fig. 6** Conductivity of  $\text{La}_{0.9-x}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$  compounds in dependence on oxygen partial pressure at 800 °C

such as free volume and critical radius, followed by an increase in activation energy for the oxide ion conduction. Furthermore, other non-structural factors like  $\text{La}^{3+}$  and anion vacancy complexes could negatively influence the total conductivity. However, particularly at  $x > 0.025$ , secondary phases influence the properties of the investigated system. We have to conclude that an A-site cation non-stoichiometric preparation is not an option to improve the electrical conductivity of the LSGM system.

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