Journal of the European Ceramic Society **19** (1999) 791–796
PII: S0955-2219(98)00315-X

0955-2219/99/$ - see front matter

Ionic/electronic Mixed Conduction Relations in Perovskite-type Oxides by Defect Structure

Helmut Ullmann,[a] Nikolai Trofimenko, A. Naoumidis,[b]* and D. Stöver[b]

[a]Technical University of Dresden, Institute of Inorganic Chemistry, 01062 Dresden, Germany
[b]Forschungszentrum Jülich GmbH, Institute for Materials and Processes in Energy Systems, 52425 Jülich, Germany

Abstract

Perovskite-type oxides $La_{1\text{-}a}A_aM_{1\text{-}b}B_bO_{3\text{-}x}$ *with* $A = Sr^{2+}$, Ln^{3+}, Ce^{4+} *and M = Fe, Co, Ga; B = Co, Fe, Mg were prepared in the concentration range* a = 0·1 *to 1 mol and* b = 0·1 *to 0·5 mol. Additionally, A-substoichiometric compositions were prepared. Preparation conditions for monophase materials and structure types of the perovskite were determined by X-ray investigation. The electrical conductivity as a function of* pO_2 *in the range* $10^5 > pO_2 > 10^{-14}$ *Pa and temperature (500 to 1000°C) was measured on ceramic shapes by a dc four-point technique in combination with solid electrolyte coulometry. The ionic part of conductivity in mixed conductors was determined by oxygen permeation measurements. The II–III-perovskites* $Sr(Co,Fe)O_{3\text{-}x}$ *in their stabilized form are excellent mixed conductors (maximum 500 S* cm^{-1} *at 400°C) and have up to 2 orders of magnitude higher oxygen ionic conductivity than the preferred III–III-perovskite* $La(Sr)Mn(Co)O_{3\text{-}x}$*. The oxygen ionic conductivity of the electrolyte* $La(Sr)Ga(Mg)O_{3\text{-}x}$*, was increased by doping with 0·1 mol Co. By applying higher Co or Fe doping concentrations the lanthanum gallate, becomes a mixed conductor. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: mixed conductors, ionic conductors, perovskites.

1 Introduction

Solid Oxide Fuel Cells (SOFCs) are practically completely ceramic devices with electronic or ionic conducting materials. The cathode is a doped $LaMnO_3$ perovskite. The electrolyte consists of yttria-stabilized zirconia (YSZ). The anode is a cermet based on YSZ with metallic nickel. Recent considerations plan the replacement of YSZ electrolyte with a perovskite based on doped $LaGaO_3$. Materials with a mixed conductivity are required to increase the electrocatalytic activity of the electrodes of an SOFC. From this point of view the investigation of this material group is attracting increasing interest.

Many of the perovskite structured oxides show a wide range of oxygen stoichiometry, indicating the tendency to ionic and electronic defect structures. These are the basis for a variety of electrical properties ranging from insulating materials through ionic to electronic conductors. Additional doping on A and B sites makes it easy to change the electrical characteristics of perovskite-type oxides. Although some of the rules of doping/property relations are known, most of the developments of new material compositions of interest for practical application have been more or less empirical. Recently Paulsen[1] published an overview. It was observed that high oxygen ionic conductivity correlates with a cubic or orthorhombic structure.[2,3] Additionally, Yokokawa[4,5] observed a strong correlation of the formation enthalpies of perovskite phases from the oxides and the Goldschmidt numbers: thermodynamic stability increases with increasing Goldschmidt number. This correlation helps to establish doping strategies, calculating with mean ionic radii in the case of doping. Unfortunately, there is a tendency that high ionic conductivity likewise correlates with low reduction stability, simply because the ionic migration requires weakly bonded ions.[6]

In this paper two examples are given for the development of perovskite-type materials of practical interest:

1.1 Strontium cobaltites

Especially the II–III cobaltites such as $SrCoO_{3\text{-}x}$ lead one to expect high concentrations of ionic defects, but they suffer from phase instability. Only their high-temperature phase is a cubic modification.[7] The high-temperature phase of $SrCoO_{3\text{-}x}$, is of cubic structure, the electronic conductivity exceeds

---

*To whom correspondence should be addressed. Fax: +49-2461-61-5700; e-mail: a.naoumidis@fz-juelich.de

the conductivity of the low-temperature phase by one order of magnitude.[7] Composition variations of this compound are now of interest as cathode materials for medium temperature SOFC. The electrocatalytic properties were investigated and discussed.

1.2 Lanthanum gallates

For years several groups searched for an ionic conductor with the perovskite structure. Finally, Ishihara[8,9] found the doped lanthanum gallates to be excellent oxygen ionic conductors. The optimum dopants and their concentrations were investigated.[8–10] For the generation of oxygen defects doping with Sr on the A-site and Mg on the B-site is performed. At lower temperatures the activation energy is increased, probably influenced by changes in ordering or structure. In this paper the variation of the type of electrical conductivity by doping of $La(Sr)Ga(Mg)O_{3-x}$, (LSGM) with some transition metal oxides was investigated and recommendations made for the application of transition- metal-doped gallates as improved electrolytes or mixed conductors.

Table 1. Calculated cell parameters from XRD data and activation energies (E_a) of investigated samples

Composition	*Prep.* T (°C) *air*	*Structure*	a (Å)	c (Å)	V_{cell} ($Å^3$)	*Temperature range (°C)*	E_a (*eV*)
$Sr_{0.9}Ce_{0.1}CoO_{3-x}$	1200	Cubic	3·849(4)	—	57·07	100–430	0·114
$Sr_{0.9}Ce_{0.1}FeO_{3-x}$	1350	Cubic	3·877(4)	—	58·31	100–430	0·187
$Sr_{0.9}Ce_{0.1}Co_{0.5}Fe_{0.5}O_{3-x}$	1200	Cubic	3·858(9)	—	57·16	100–400	0·122
$Sr_{0.9}La_{0.1}Co_{0.5}Fe_{0.5}O_{3-x}$	1200	Cubic	3·849(8)	—	57·06	100–400	0·074
$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-x}$	1450	Cubic	3·905(0)	—	59·55	450–620	0·981
						700–1000	0·727
$La_{0.9}Sr_{0.1}(Ga_{0.9}Fe_{0.1})_{0.8}Mg_{0.2}O_{3-x}$	1450	Cubic	3·901(9)	—	59·40	450–1000	0·657
$La_{0.9}Sr_{0.1}(Ga_{0.8}Fe_{02})_{0.8}Mg_{0.2}O_{3-x}$	1450	Cubic	3·986(5)	—	59·16	300–1000	0·368
$La_{0.9}Sr_{0.1}(Ga_{0.7}Fe_{0.3})_{0.8}Mg_{0.2}O_{3-x}$	1450	Cubic	3·895(9)	—	59·13	300–570	0·311
$La_{0.85}Sr_{0.1}(Ga_{0.9}Fe_{0.1})_{0.8}Mg_{0.2}O_{3-x}$	1450	Cubic	3·895(7)	—	59·12	450–1000	0·578
$La_{0.9}Sr_{0.1}(Ga_{0.9}Co_{0.1})_{0.8}Mg_{0.2})_{3-x}$	1450	Cubic	3·895(2)	—	59·10	450–1000	0·707
$La_{0.9}Sr_{0.1}(Ga_{0.8}Co_{0.2})_{0.8}Mg_{0.2}O_{3-x}$	1450	Hexagonal	5·501(0)	13·345(9)	349·76	450–670	0·433
						670–1000	0·310
$La_{0.9}Sr_{0.1}(Ga_{0.75}Co_{0.25})_{0.8}Mg_{0.2}O_{3-x}$	1450	Hexagonal	5·495(4)	13·341(2)	348·92	100–450	0·231
						670–1000	0·192
$La_{0.9}Sr_{0.1}(Ga_{0.7}Co_{0.3})_{0.8}Mg_{0.2}O_{3-x}$	1450	Hexagonal	5·495(0)	13·312(8)	348·12	100–450	0·201
						500–780	0·265
$La_{0.85}Sr_{0.1}(Ga_{0.9}Co_{0.1})_{0.8}Mg_{0.2}O_{3-x}$	1450	Hexagonal	5·507(8)	13·365(5)	351·13	450–1000	0·694
$La_{0.9}Sr_{0.1}Ga_{0.9}Co_{0.1}O_{3-x}$	1450	Hexagonal	5·497(7)	13·306(3)	348·30	—	—
$La_{0.9}Sr_{0.1}(Ga_{0.9}Co_{0.1})_{0.9}Mg_{0.1}O_{3-x}$	1450	Hexagonal	5·497(3)	13·303(4)	348·17	—	—

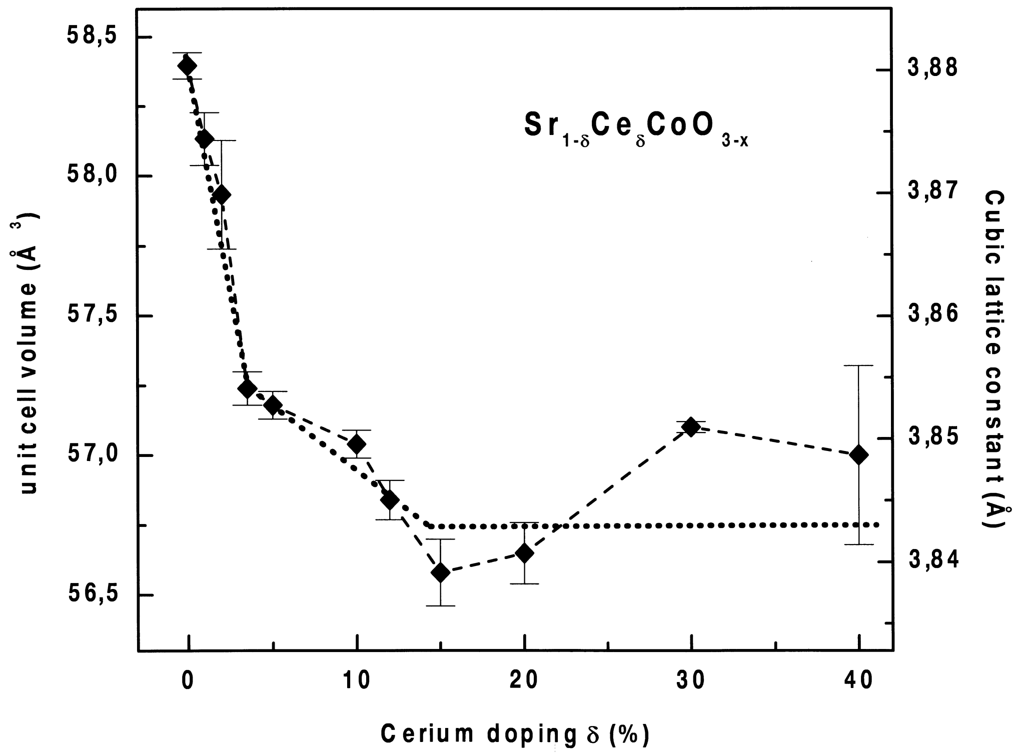

Fig. 1. Cubic phase formation versus dopant concentration for samples prepared at 1200°C in air: lattice parameters of the perovskite phase $Sr_{1-\delta}Ce_{\delta}CoO_{3-x}$.

2 Experimental Techniques

2.1 Sample preparation

The initial compounds $SrCO_3$, CeO_2, Co_3O_4 and Fe_2O_3 (99·9% purity) were mixed in a mortar and then reacted at 1000°C for 30 h in air. After cooling the products were cracked and ground for 2 h, followed by heating at 1100°C for 10 h. Ceramic shapes were pressed without binder, sintered in air at 1200°C for 15 h with heating and cooling rates of 1°C min^{-1}. At higher iron contents reaction and sintering was performed at 1350°C.

Samples of LSGM were prepared by mixing $SrCO_3$, $MgCO_3$, Ga_2O_3 and La_2O_3 (99·9% purity) and solid-state reaction at 1350°C/48 h in air. Ceramic shapes were sintered at 1450°C/20 h in air.

All sample densities after pycnometric results were greater than 93% of the theoretical value, calculated from unit cell volumes.

After that preparation, within the ranges of existence of the perovskite phase (see Section 3) no second phases were observed in X-ray diffraction with Siemens D5000 equipment. $La_{0{\cdot}9}Sr_{0{\cdot}1}Ga_{0{\cdot}8}Mg_{0{\cdot}2}O_{3\text{-}x}$ displays a white-brown color, all phases doped with transition metals were of a black color. Modifications of the perovskite structure, lattice constants and cell volumes are given in Table 1.

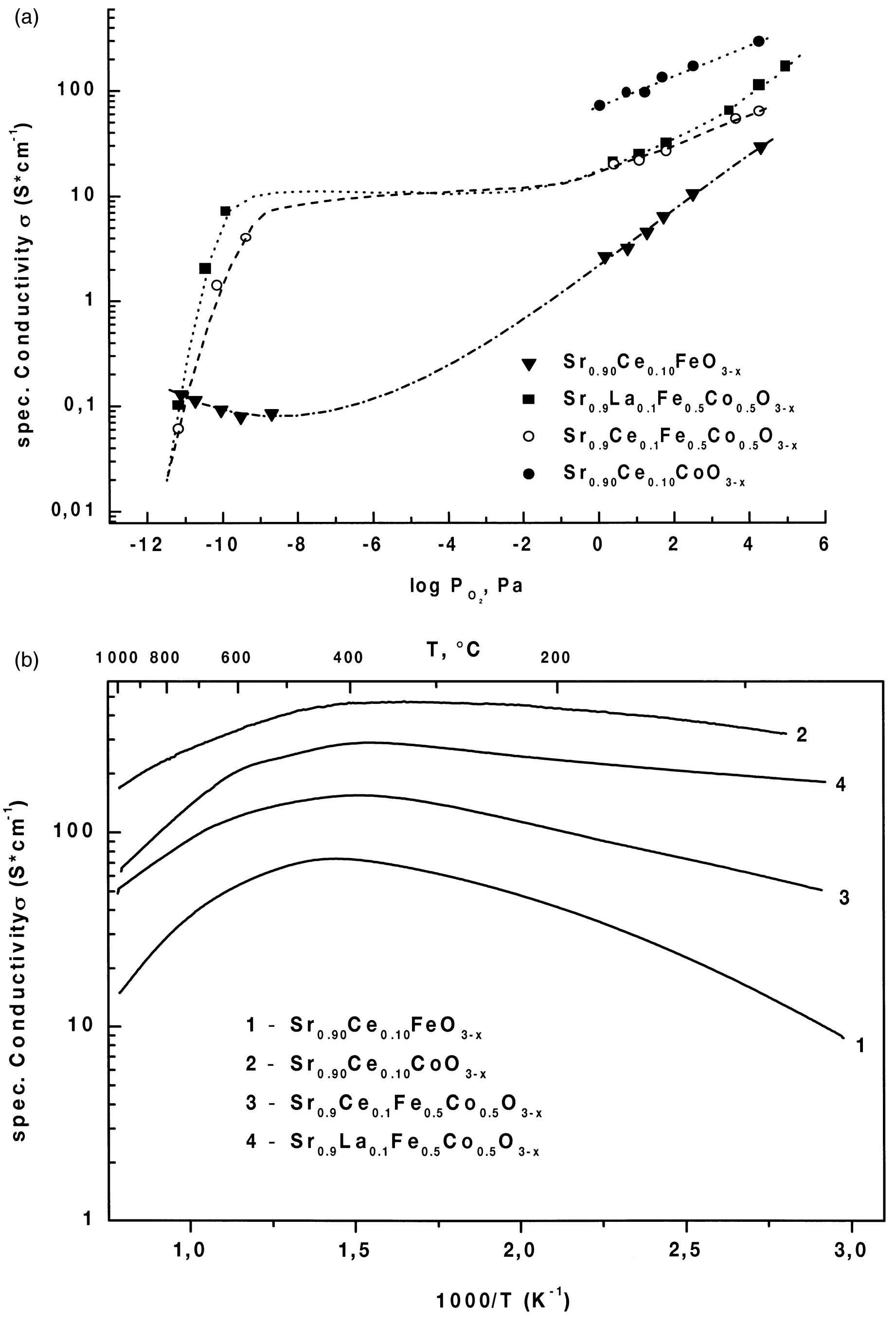

Fig. 2. Electrical conductivity of $Sr(La,Ce)Co((Fe)O_{3\text{-}x}$: (a) versus oxygen partial pressure at 800°C; (b) conductivity–temperature relation in air.

The powders reacted in a temperature-programmed furnace with a gas of oxygen partial pressures controlled by the OXYLYT device (SensoTech Magdeburg).[11]

The electrical conductivity was measured on sintered shapes of 2×4×10 mm size, during pressing the shapes were equipped with four Pt-wires of 0·1 mm diameter. For the cobaltite/ferrate samples with high electronic conductivity, a dc four-point technique was used. For the gallates with high ionic conductivity, ac impedance measurement (average 50 kHz) was preferred. where the impedance became independent from pO_2. Oxygen permeation measurements were performed on polished pellets (10×1 mm), hermetically fixed by a gold ring seal into the end of an alumina tube. The two surfaces of the pellet were exposed to gas flows with different oxygen partial pressures, controlled by the OXYLYT. The permeation flux of oxygen from the high to the low pressure side was measured by the solid electrolyte technique.

3 Phase Formation and Stability

3.1 Strontium cobaltites/ferrates

The cubic high-temperature modification of $SrCoO_{3-x}$ and $SrFeO_{3-x}$ is stabilized by Ce or La

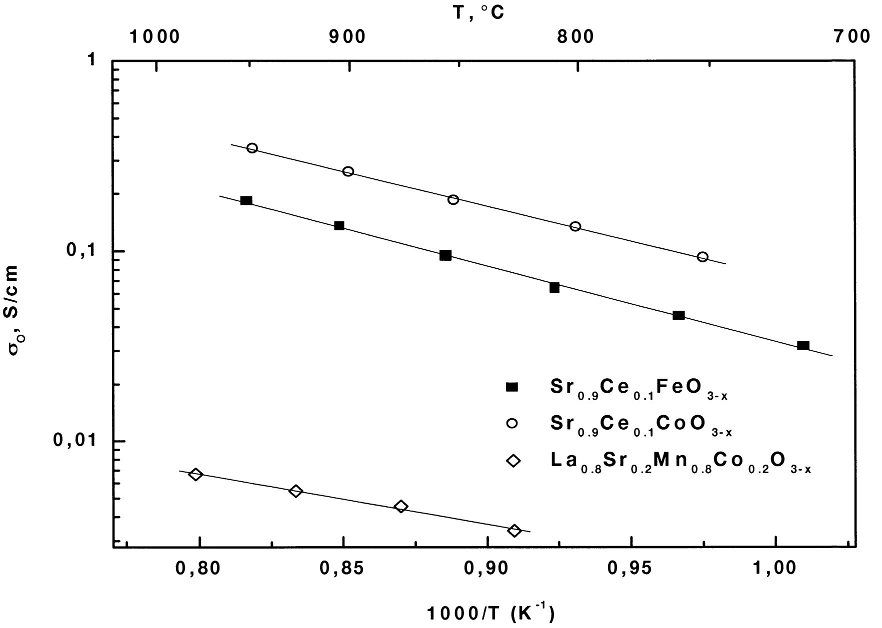

Fig. 3. Oxygen permeation as a measure of oxygen ionic conductivity. Calculated oxygen ionic conductivity for II–III-perovskites in comparison to the ionic conductivity of a III–III-perovskite.

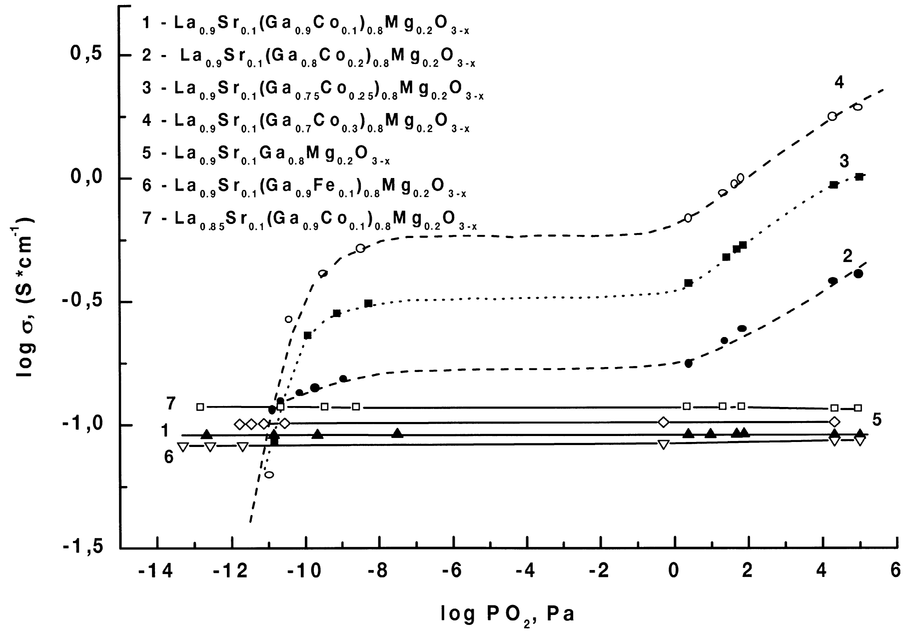

Fig. 4. Electrical conductivity of $La_{0.9}Sr_{0.1}(Ga_{1-y}M_y)_{0.8}Mg_{0.2}O_{3-x}$ versus oxygen partial pressure at 800°C as function of dopant concentration y. M = Fe, Co $y = 0$ to 0·03.

doping. The solubility of the dopant on the A-site in the monophase perovskite is limited to about 15 mol%, as shown by the breaks in the lattice constant–doping concentration dependence (Fig. 1). The La is 3+, the Ce on the A-site is assumed to be forced into the 3+ state with a tendency to the less voluminous Ce^{4+} ion.

Cobalt-containing perovskites are less reduction-stable compared with the manganites or ferrates, thus fact should result in high oxygen ionic mobility.[6] The reduction mechanism of III–III-perovskites (a) differs from that of the II-III-perovskites (b):

$$2LaCo^{III}O_3 \rightarrow La_2Co^{II}O_4 + Co^{II}O + O_2$$

$$La_2Co^{II}O_4 \rightarrow La_2O_3 + CoO$$

$$SrCo^{III}O_{2\cdot5} \rightarrow SrO + Co^{II}O + 1/4\ O_2$$

Depending on pO_2 and temperature the reduction may end in the formation of metallic cobalt.

3.2 Doped lanthanum gallates

$La_{0\cdot9}Sr_{0\cdot1}\ (Ga_{1-y}M_y)_{0\cdot8}Mg_{0\cdot2}O_{3-x}$ with the dopants M = Fe, Co and $y = 0$ to 0·3 mol in the air-oxidized state show cubic and hexagonal perovskite phases (Table 1). The cubic phase is preferred at lower doping concentrations (Co up to 0·1 mol) and by the more reduction-stable Fe-doped oxides (up to 0·3 mol). The ionic radii of the +4 and +3 cations are very similar to that of Ga^{3+}, whereas the Co^{2+} differs more from Ga^{3+}. No second crystal phases could be detected, even after reduction (10^{-12} Pa O_2/800°C). It should be noted that the concentration of Mg also plays an important role in the solubility of Co into the lattice: second phases such as $LaSrGaO_4$ and La_4SrO_7 were detected in all samples with a Mg content lower than 0·2 mol.

4 Electronic and Oxygen Ionic Conductivity

4.1 Strontium cobaltites/ferrates

The total electrical conductivity [Fig. 2(a)] of the strontium cobaltites/ferrates decreases with decreasing oxygen partial pressures, indicating p-type semiconductivity. $Sr_{0\cdot9}Ce_{0\cdot1}CoO_{3-x}$ decomposes below $pO_2 < 10^{-1}$ Pa, Co containing ferrates below 10^{-10} Pa oxygen. Increasing substitution of Co by Fe stabilizes the perovskite oxide, pure ferrate changes the conductivity below 10^{-8} Pa O_2 to n-type.

The temperature dependence of the conductivity [Fig. 2(b)] demonstrates increasing conductivities with temperature up to a maximum at about 400°C, indicating thermally activated p-type semiconductivity (Table 1), which changes to metallic conduction behaviour above the maximum. Activation energies up to 400°C are in the range of 0·1 to 0·2 eV. Maximum values of conductivity are 500 S cm^{-1} for $Sr_{0\cdot9}Ce_{0\cdot1}CoO_{3-x}$, the conductivity of the other compositions decreases with increasing substitution of Co by Fe. This is an expression of growing reduction stability, that means lower concentration of oxygen vacancies. Replacing the Ce by La on the A-site leads to improved conductivity.

The oxygen ionic conductivity of this type of mixed conducting oxides is some orders of magni-

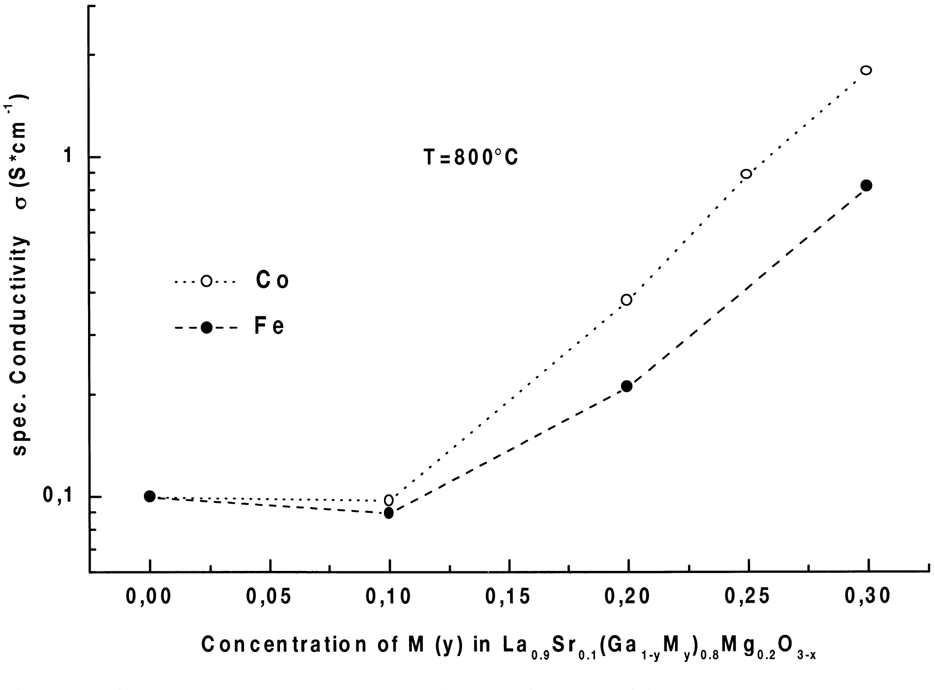

Fig. 5. Electrical conductivity of $La_{0\cdot9}Sr_{0\cdot1}(Ga_{1-y}M_y)_{0\cdot8}Mg_{0\cdot2}O_{3-x}$ in air as function of dopant concentration y. M = Fe, Co y = 0 to 0·30.

tude lower than the electronic conductivity. In this case, the measurement of the permeation flux of oxygen through a ceramic membrane in an oxygen partial pressure gradient is a key to the calculation of oxygen diffusion and oxygen ionic conductivity. The ionic current density j_{ion} is an expression of the ionic conductivity and the driving force, the relation of oxygen partial pressures divided by the membrane thickness L. The ionic current density is calculated from the partial pressures in test gas at the inlet and outlet and the flow rate of this gas. Sources of errors in these measurements are sufficient, nevertheless, the first results (Fig. 3) show a clear tendency: for comparison the oxygen ionic conductivity of the preferred cathode material of doped lanthanum manganite is depicted. The oxygen ionic conductivity of the II–III-perovskites is up to 2 orders of magnitude higher, even higher than the conductivity of YSZ.

4.2 Lanthanum gallates

The fact that conductivity is independent on oxygen partial pressure (Fig. 4) for the 0·1 mol cobalt- and iron-substituted gallates is a sign of dominating ionic transfer over the whole pO_2 range from air to hydrogen-containing gas. The conductivity at 800°C increases from Fe to Co at 0·1 mol concentrations at the Ga site, indicating the influence of enhanced oxygen defect concentrations in this raw. The conductivity values of the well-known[8–10,12] $La_{0\cdot 9}Sr_{0\cdot 1}Ga_{0\cdot 8}Mg_{0\cdot 2}O_{3\text{-}x}$ (LSGM) were considerably exceeded by the A-sub-stoichiometric composition $La_{0\cdot 85}Sr_{0\cdot 1}(Ga_{0\cdot 9}Co_{0\cdot 1})_{0\cdot 8}\text{-}Mg_{0\cdot 2}O_{3\text{-}x}$ (LSGCM).

Increasing cobalt or iron content led to increased p-type conductivity. For cobalt, this is in agreement with a cubic to hexagonal phase transformation observed at 0·1 mol (Fig. 5). The p-type conductivity of the hexagonal phases is characterized by considerably lower activation energies compared to the ionic conductivity (see Table 1).

Within the range of ionic conductivity regime the temperature dependence shows a break in activation energy for LSGM near 700°C, This can be discussed as order–disorder or phase transformation from cubic at high-temperature to rhombohedral at low temperature, which was observed in doped praseodymium gallates.[13] For the ionic conductivity of LSGCM and LSGFM ($y = 0{\cdot}1$) a change in activation energy could not be observed. In this case, the low values of activation energy at high temperature were observed down to 400°C. Due to this fact the conductivity values of the Co and Fe ($y = 0{\cdot}1$) substituted LSGM especially below 700°C exceed the values of nonsubstituted LSGM, and even of $Ce(Gd)O_{2\text{-}x}$.

5 Prospects for Application

At elevated temperatures the high oxygen ionic and electronic conductivities make the II–III-perovskite oxides attractive candidate materials for several important applications, including solid oxide fuel cell electrodes and electrolytes, oxygen separation membranes and catalytic membrane reactors for partial oxidation of natural gas. Especially the strontium cobaltites/ferrates with their high oxygen ionic conductivity and very high electronic conductivity are applicable at remarkably lower temperatures than the well-known lanthanum manganites.

For solid oxide fuel cell application at medium temperatures, a combination of the strontium cobaltites/ferrates with lanthanum gallate electrolytes seems to be of interest because of the positive influence of lower cobalt contents in the latter materials.

References

1. Paulsen, J., Thermodynamics, oxygen stoichiometric effects and transport properties of ceramic materials in the system Sr–Ce–M–O (M=Co, Fe), Ph.D. thesis, Technical University of Dresden, 1998.
2. Butler, V., Catlow, C. R., Fender, B. E. F. and Harding, J. H., Dopand ion radius and ionic conductivity in cerium dioxide. *Solid State Ionics*, 1982, **8**, 109–113.
3. Cook, R. L. and Sammells, A. F., On the systematic selection of perovskite solid electrolytes for intermediate temperature fuel cells. *Solid State Ionics*, 1991, **45**, 311–321.
4. Yokokawa, H., Sakai, N., Kawada, T. and Dokiya, M., Thermodynamic stabilities of perovskite oxides for electrodes and other electrochemical materials. *Solid State Ionics*, 1992, **52**, 43–56.
5. Yokokawa, H., Kawada, T. and Dokiya, M., Thermodynamic regularitities in perovskite and K_2NiF_4 compounds. *J. Am. Ceram. Soc.*, 1989, **72**, 152–153.
6. Weppner, W., Materials and concepts for solid state electromechanical devices. Fast Ion Transport in Solids, NATO ASI Series E, Applied Sciences Vol. 250. B. Scrosati, A. Magistris, C. M. Mari and G. Mariotto (eds.), Klewer Academic Publishers, Dordrecht, NL, 1992, pp. 9–39.
7. Vashook, V. V., Zinkevich, M. V., Ullmann, H., Paulsen, J., Trofimenko, N. and Teske, K., Oxygen non-stoichiometry and electrical conductivity of the binary strontium cobalt oxide $SrCoO_4$. *Solid State Ionics*, 1997, **99**, 23–32.
8. Ishihara, T., Matsuda, H. and Takita, Y., Doped $LaGaO_3$ perovskite type oxide as a new oxide ion conductor. *J. Am. Chem. Soc.*, 1994, **116**, 3801–3803.
9. Ishihara, T., Matsuda, H. and Takita, Y., Effects of rare earth cations doped for La site on the oxide ionic conductivity of $LaGaO_3$-based perovskite type oxide. *Solid State Ionics*, 1995, **79**, 147–151.
10. Huang, Peng-nian and Petric, A., Superior oxygen ion conductivity of lanthanum gallate doped with strontium and magnesium. *J. Electrochem. Soc.*, 1996, **143**, 1644–1648.
11. Teske, K., Ullmann, H. and Trofimenko, N., Thernal analysis of transition metal and rare earth oxide system—gas interactions by a solid electrolyte—based coulometric technique. *J. of Thermal Analysis*, 1997, **49**, 1211–1220.
12. Furutani, Y., Ishihara, T., Nishiguchi, H. and Takita, Y., Oxide ion conductivity of doped $PrGaO_5$ perovskite oxide, Fifth Internat. Symp. SOFC–V, Aachen, Germany 1997, Electrochem. Proc. Vol. 97–40, 1997, 1086–1095.