Journal of the European Ceramic Society 21 (2001) 1817–1820

www.elsevier.com/locate/jeurceramsoc

Correlation between the defect structure, conductivity and chemical stability of $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ cathodes for SOFC

Danjela Kuščer *, Janez Holc, Marko Hrovat, Drago Kolar

Jozef Stefan Institute, University of Ljubljana, Jamova 39, 61000 Ljubljana, Slovenia

Received 4 September 2000; received in revised form 14 November 2000; accepted 20 November 2000

Abstract

The chemical compatibility of a $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ cathode and an yttria-stabilised ZrO_2 electrolyte (YSZ) was studied for solid-oxide fuel cell (SOFC) applications. The Al addition to the $LaFe_{1-x}Al_xO_3$ reduces the reactivity with the YSZ associated with increasing tolerance factor. The Sr addition to the $LaFe_{1-x}Al_xO_3$ leads to Fe^{4+} and anion-vacancy formation. The Sr addition hinders the formation of $La_2Zr_2O_7$, but at $y \geqslant 0.2$ promotes the formation of $SrZrO_3$ at the $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$/YSZ interface. At low $p(O_2)$ the formation of secondary phases is pronounced what could be related to the formation of anion vacancy. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Defects; Electrical conductivity; Fuel cells; Perovskites; X-ray methods

1. Introduction

In solid-oxide fuel cells (SOFCs) $LaMnO_{3\pm\delta}$-based perovskites are currently used as the cathodes, and ZrO_2 containing 8 mol% Y_2O_3 (YSZ) as the solid electrolyte. The main disadvantage of a $LaMnO_{3\pm\delta}$-based cathode is its incompatibility with the solid electrolyte. At the operating temperature of ~1000°C, high-impedance layers ($La_2Zr_2O_7$ and $SrZrO_3$) are formed at the cathode/electrolyte interface, lowering the fuel-cell efficiency. As a result, other conductive oxides are being investigated as possible SOFC cathodes.

Yokokawa et al.[1] studied the chemical stability of perovskite compounds in terms of stabilisation energy, which is strongly related to the Goldschmidt tolerance factor t. This factor describes the geometrical matching between ions in a perovskite lattice and reaches the value of 1 when the matching is ideal. Simultaneously, the compounds with $t \approx 1$ exhibit a large stabilisation energy. On the basis of the stabilisation energy it was theoretically shown that $LaFeO_3$ and YSZ would not form $La_2Zr_2O_7$.[1]

$LaFeO_3$ is stable in the oxygen partial pressure $p(O_2)$ range from 1 to $10^{-13}\times 63$ bar at 1200°C.[2] At room temperature in air $LaFeO_3$ has an orthorhombic structure and up to 845°C no phase transition has been observed.[3] In air up to 1200°C, $LaFeO_3$ has no anion vacancies in its structure and all iron ions are in the valence state 3+.[4] At low oxygen partial pressures, the Fe^{2+} and anion vacancies are formed. $LaFeO_3$ is a hopping-type conductor with a conductivity of 0.5 S/cm at 900°C in air.[5] At the SOFCs' operating temperature a conductivity of at least 100 S/cm is required for the cathode materials. The lack of conductivity limits the use of $LaFeO_3$ as a cathode in a SOFC. The conductivity of $LaFeO_3$ is increased with addition of Sr and results in the formation of Fe^{4+} and anion vacancies.[4]

This paper is focused on the correlation between the defect structure and conductivity of $LaFeO_3$-based perovskites. The chemical compatibility of $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ and YSZ is discussed in relation to the defect structure.

2. Experimental

$La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ ($0 \leqslant x \leqslant 1$, $0 \leqslant y \leqslant 1$) solid solutions were synthesised by a solid-state reaction from

---

* Corresponding author. Tel.: +386-1-477-3489; fax: +386-1-426-3126.

E-mail address: danjela.kuscer@ijs.si (D. Kuščer).

0955-2219/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(01)00122-4

$La(OH)_3$ (Ventron, 99.9%), Fe_2O_3 (Alfa, 99.9%), Al_2O_3 (Alcoa, A — 16, +99%) and $SrCO_3$ (Ventron, 99.9%) materials. The powders were homogenised, pressed into pellets and fired at 1300°C for up to 100 h in air.

The single-phase materials were characterised at room temperature by X-ray powder diffraction analysis (XRD) using a Philips PW 1710 diffractometer with Cu–K_α radiation. Cell parameters were calculated by the least-squares method.

The amount of Fe^{4+} ions in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ was determined by Mössbauer spectroscopy. All measurements were conducted using standard transmission geometry. A constant acceleration spectrometer with a $^{57}Co/Rh$ source was used for the experiment. The spectra were fitted to the sum of the Lorentzians by a least-squares-refinement method.

The conductivity of sintered pellets with diameter 6 mm and thickness 4 mm was measured using the four-point method with a Keithley 196 multimeter and a Keithley 580 Micro-ohmmeter in the temperature range from 20 to 900°C in air and in nitrogen. Unfritted Pt electrodes (Demetron M 8014) were used as contacts.

For the compatibility study a 1:1 mass ratio of the $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ and YSZ (ZrO_2 8 mol% Y_2O_3, Tosoh, >99%) powders were homogenised, pressed into pellets and fired at 1200°C for 30 h in air or in nitrogen [$p(O_2) = 50$ Pa]. After heat treatment the pellets were analysed by X-ray powder diffraction analysis.

Diffusion couples were prepared from presintered $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ and YSZ pellets, which were hot pressed at 1300°C for 15 h in air. A scanning electron microscope (SEM) Jeol-JXA 840 equipped with a Tracor-Northern energy dispersive system (EDS) was used for overall microstructural and compositional analysis.

3. Results and discussion

The chemical compatibility of cathode materials and YSZ was evaluated in terms of a tolerance factor. The calculated tolerance factor (t) for $LaFeO_3$ is 0.957. A higher tolerance factor should lower the reactivity with YSZ,[1] therefore, materials with a higher tolerance factor than $LaFeO_3$ were estimated. $LaAlO_3$ is a suitable material not only because its calculated tolerance factor (t) is 1.02 but also because $LaAlO_3$ and $LaFeO_3$ form solid solutions of $LaFe_{1-x}Al_xO_3$ across the whole composition range $0 \leqslant x \leqslant 1$ at 1300°C.[6]

In the $LaFe_{1-x}Al_xO_3$ perovskite structure Al ions are incorporated onto Fe sites according to Shannon's radii size [$r(Al^{3+}) = 0.053$ nm, $r(Fe^{3+}) = 0.064$ nm].[7] Mössbauer spectroscopy showed that all the iron ions in $LaFe_{1-x}Al_xO_3$ are in the 3+ valence state and no anion vacancies are observed in the structure in air up to 1200°C. As a consequence, the total conductivity of $LaFe_{1-x}Al_xO_3$ decreases with increasing Al content.[8]

The X-ray powder diffraction analysis shows that $LaFeO_3$ and YSZ do not form any reaction products in air at 1200°C after 30 h. However, $La_2Zr_2O_7$ formation was observed in the $LaFeO_3$/YSZ mixture fired in nitrogen [$p(O_2) = 50$ Pa] at 1200°C after 30 h (Fig. 1).

The X-ray powder diffraction analysis showed no reaction products formed between $LaAlO_3$ ($t = 1.0$) and YSZ nor between a $LaFe_{0.7}Al_{0.3}O_3$ ($t = 0.97$) and YSZ mixture, both fired in air at 1200°C for 30 h. After firing in nitrogen, $La_2Zr_2O_7$ was formed from $LaFe_{0.7}Al_{0.3}O_3$ and YSZ, whereas no reaction products were observed with the $LaAlO_3$ and YSZ mixture (Fig. 2). From the results it appears that the formation of secondary phase is pronounced at low oxygen partial pressure (e.g. in nitrogen) and that $LaAlO_3$ hinders $La_2Zr_2O_7$ formation,

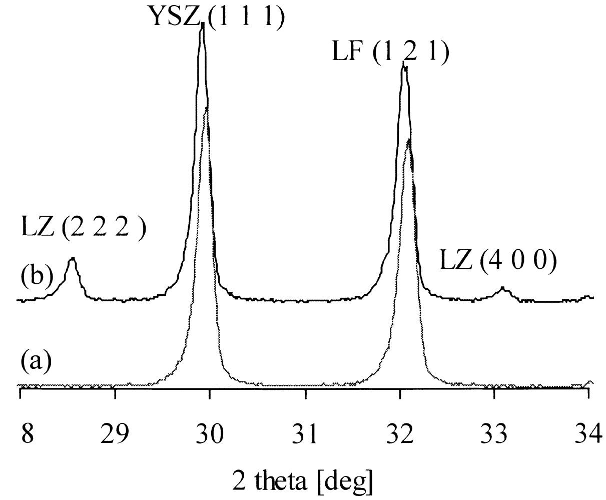

Fig. 1. $LaFeO_3$/YSZ mixture fired at 1200°C for 30 h in (a) air (b) nitrogen. The formation of $La_2Zr_2O_7$ was observed in nitrogen. LF — $LaFeO_3$, LZ — $La_2Zr_2O_7$.

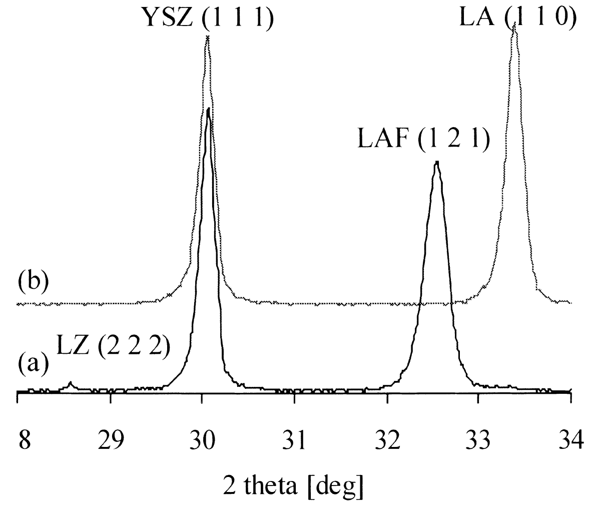

Fig. 2. $LaFe_{0.7}Al_{0.3}O_3$/YSZ (a) and $LaAlO_3$/YSZ (b) mixture fired at 1200°C for 30 h in nitrogen. The $La_2Zr_2O_7$ was detected in $LaFe_{0.7}Al_{0.3}O_3$. LAF — $LaFe_{0.7}Al_{0.3}O_3$, LA — $LaAlO_3$, LZ — $La_2Zr_2O_7$.

which is in agreement with the thermodynamic predictions reported by Yokokawa.[1]

In order to understand the diffusion processes between cathode and YSZ, the unit-cell parameters of $LaFe_{1-x}Al_xO_3$ were calculated after the firing of the $LaFe_{1-x}Al_xO_3$/YSZ mixtures. It has been reported that the unit-cell volume of $LaFeO_3$ changes if the structure is modified with other ions, i.e. Co^{3+}.[9] The unit-cell volume of $LaFeO_3$ fired in air and in nitrogen is 0.2430(2) nm^3 and 0.2433(2) nm^3, respectively, and is within experimental error practically the same. The unit-cell volume of $LaFeO_3$ fired with YSZ in air is 0.2436(7) nm^3 and in nitrogen, where the $La_2Zr_2O_7$ formation was the most evident, 0.2444(5) nm^3. The slight unit-cell expansion is attributed to the diffusion of Zr and/or Y ions into $LaFeO_3$.

This is in agreement with the results obtained by electron microscopy for the $LaFe_{1-x}Al_xO_3$/YSZ diffusion couple fired at 1300°C in air. The temperature of 1300°C is sufficient for a 2 μm layer of $La_2Zr_2O_7$ to be formed at the $LaFeO_3$/YSZ interface, whereas no reaction products were detected in the $LaFe_{0.7}Al_{0.3}O_3$/YSZ mixture.[10] Fig. 3 shows the quantitative distribution of the elements in the $LaFeO_3$/YSZ diffusion couple indicating considerable interdiffusion between $LaFeO_3$ and YSZ in air at 1300°C. Zr ions diffuse up to 5 μm into $LaFeO_3$, whereas La and Fe ions are detected at the distance of up to 10 μm in the YSZ. In $La_2Zr_2O_7$, Fe ions are detected. The Y distribution was not determined by EDS analysis because the characteristic lines of Y and Zr overlap. There is no data concerning the solubility of ZrO_2 in $LaFe_{1-x}Al_xO_3$, but it is known that at 1300°C in air the solubility of La_2O_3 in ZrO_2 is up to 2% and for Fe_3O_4 in ZrO_2 up to 5%.[11,12] The solubility of Al_2O_3 in ZrO_2 was shown to be negligible.[13] According to results obtained by EDS analysis it seems that the expansion of the unit-cell volume of $LaFeO_3$ is a consequence of the diffusivity of Zr ions into $LaFeO_3$. The ionic radius of Zr^{4+} [$r=0.072$ nm] is bigger than Fe^{3+} [$r=0.064$ nm][7] and consequently it is expected that the lattice parameters of $LaFeO_3$ would expand.

Mizusaki et al.[4] reported that in $La_{1-y}Sr_yFeO_{3-\delta}$ the concentration of anion vacancies increases and the Fe^{4+} concentration decreases with increasing Sr content and with increasing temperature. The results obtained by Mössbauer spectroscopy show that the incorporation of Sr into $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ causes a charge imbalance leading to Fe^{4+} and anion-vacancy formation. The total conductivity depends on Fe^{4+}/Fe^{3+} ratio in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$. For $La_{1-y}Sr_yFe_{0.7}Al_{0.3}O_{3-\delta}$ perovskites the total conductivity exhibits maximum at $y=0.2$ in air in temperature range from 20 to 900°C.[6]

For the compatibility study the powder mixture of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ and YSZ was fired at 1200°C for 30 h in air and in nitrogen. The results obtained by X-ray powder diffraction analysis show that $SrZrO_3$ was formed in air as well as in nitrogen. The $La_2Zr_2O_7$ phase was not detected. Similar results were obtained for the $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$/YSZ diffusion couple fired in air at 1300°C. The quantitative distribution of the elements for the $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$/YSZ is shown in Fig. 4. EDS analysis indicates considerable interdiffusion between $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ and YSZ. La, Fe and Sr ions diffuse into the YSZ and the Zr ions diffuse into the $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ perovskite phase what coincides with the literature data concerning solubility. The solid-solubility limits of La_2O_3, SrO, Fe_2O_3 and Al_2O_3 into ZrO_2 is up to 2,[11] 2.5,[14] 5[12] and 0[13] mol% at 1300°C in air, respectively. There is no data concerning the solubility of ZrO_2 and Y_2O_3 in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$. In $SrZrO_3$, La and Fe ions are detected. Al ions were detected neither in the YSZ nor in the $SrZrO_3$.

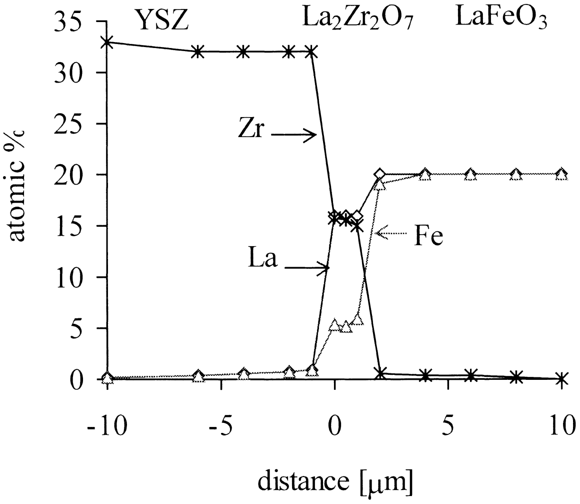

Fig. 3. Quantitative distribution of the elements in the $LaFeO_3$/YSZ diffusion couple, fired at 1300°C for 15 h in air.

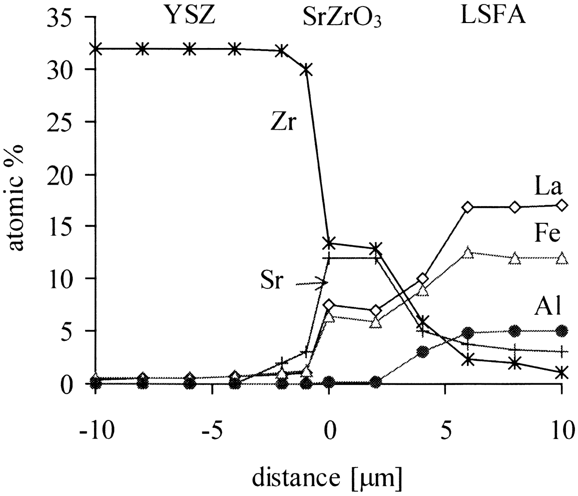

Fig. 4. Quantitative distribution of the elements in the $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$/YSZ diffusion couple, fired at 1300°C for 15 h in air. LSFA — $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$.

The distribution of Y was not shown, because the characteristic lines of Y, Sr and Zr overlap.

The lattice parameters of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ fired with YSZ at 1200°C in air and in nitrogen were calculated. The unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ fired in air is 0.3450(9) nm^3 and it is expanded when it is fired with YSZ in air [0.3554(6) nm^3]. In nitrogen, the unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ is 0.3516(4) nm^3 and the unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ fired with YSZ in nitrogen is 0.3590(5) nm^3. The unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ fired in nitrogen is higher then that in air [$V_{\mathrm{air}} = 0.3450(9)$ nm^3, $V_{\mathrm{nitrogen}} = 0.3516(4)$ nm^3]. Mizusaki et al.[4] reported that the concentration of anion vacancies in $La_{1-y}Sr_yFeO_{3-\delta}$ increases with decreasing oxygen partial pressure. The increase in unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ in nitrogen could be a consequence of anion vacancy formation at low oxygen partial pressure leading to increase in lattice parameters.

The considerable expansion of the unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ fired with YSZ in air as well as in nitrogen could originate from the dissolution of Zr ions into the perovskite lattice, which agrees with the EDS analysis performed on the $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$/YSZ diffusion couple. The ionic radius of Zr^{4+} is bigger than that of iron ions [$r(Zr^{4+}) = 0.72$ nm, $r(Fe^{3+}) = 0.064$ nm, $r(Fe^{4+}) = 0.0585$ nm][7] and therefore the expansion of the lattice parameters is expected.

The addition of Sr into $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ hinders the formation of $La_2Zr_2O_7$, but promotes the formation of $SrZrO_3$ at 1200°C in air as well as in nitrogen. It seems that the concentration of secondary phase $SrZrO_3$ in $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$/YSZ mixture in air and in nitrogen does not distinguish significantly. The influence of oxygen partial pressure on reactivity between cathode and YSZ is less prominent in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ than in $LaFe_{1-x}Al_xO_3$.

The formation of secondary phases and considerable interdiffusion between the perovskites: $LaFeO_3$, $LaFe_{0.7}Al_{0.3}O_3$, $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ and YSZ, demonstrate that they are not coexistent phases.

4. Conclusion

$La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ solid solutions were evaluated as a possible cathode material for solid-oxide fuel cells. The present investigation has revealed that the secondary phases $La_2Zr_2O_7$ and $SrZrO_3$ should formed between $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ cathode and yttrium-stabilised ZrO_2 solid electrolyte what depends on Sr and Al content in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$, on oxygen partial pressure and temperature. At 1200°C in $LaFe_{1-x}Al_xO_3$/YSZ mixture no reaction products were observed in air and in nitrogen in $LaAlO_3$/YSZ mixture whereas $La_2Zr_2O_7$ was formed in $LaFeO_3$/YSZ and $LaFe_{0.7}Al_{0.3}O_3$/YSZ mixtures in nitrogen. $SrZrO_3$ was formed between $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ and YSZ at 1200°C in air and in nitrogen.

The unit-cell volume of $La_{0.8}Sr_{0.2}Fe_{0.7}Al_{0.3}O_{3-\delta}$ expands when it is fired with YSZ at 1200°C in air and in nitrogen. This coincides with EDS analysis which shows considerable interdiffusion between $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ and YSZ. The Al addition and firing at high oxygen partial pressure hinders the reaction between $LaFe_{1-x}Al_xO_3$ and YSZ. The Sr addition in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ promotes the $SrZrO_3$ formation. The influence of atmosphere on reactivity between cathode and YSZ is less prominent in $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$ than in $LaFe_{1-x}Al_xO_3$.

References

1. 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.
2. Nakamura, T., Petzow, G. and Gauckler, L. J., Stability of the perovskite phase $LaBO_3$ (B = V, Cr, Mn, Fe, Co, Ni) in reducing atmosphere. *Mater. Res. Bull.*, 1979, **14**, 649–659.
3. Geller, S. and Wood, E. A., Crystallographic studies of perovskite-like compounds. I. Rare earth ortoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$. *Acta Crystallogr.*, 1956, **9**, 563–568.
4. Mizusaki, J., Yoshihiro, M., Yamauchi, S. and Fueki, K., Nonstoichiometry and defect structure of the perovskite-type oxides $La_{1-x}Sr_xFeO_{3-\delta}$. *J. Solid State Chem.*, 1985, **58**, 257–266.
5. Holc, J., Kuščer, D., Hrovat, M., Bernik, S. and Kolar, D., Electrical and microstructural characterisation of $La_{0.8}Sr_{0.2}Fe_{1-x}Al_xO_3$ and $La_{0.8}Sr_{0.2}Mn_{1-x}Al_xO_3$ as possible SOFC cathode materials. *Solid State Ionics*, 1997, **95**, 259–268.
6. Kuščer, D., Hanžel, D., Holc, J., Hrovat, M. and Kolar, D., Defect structure and electrical properties of $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$. *J. Am. Ceram. Soc.*, in press.
7. Shannon, R. D., Revisited effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, 1976, **A 32**, 751–767.
8. Kuščer, D., Dimc, F., Holc, J., Hrovat, M., Bernik, S. and Kolar, D., Electrical and microstructural characterisation of Al_2O_3 doped $LaFeO_3$. *J. Mater. Sci. Lett.*, 1996, **15**, 974–976.
9. Tai, L. W., Nasrallah, M. N., Anderson, H. U., Sparlin, D. M. and Sehlin, S. R., Structure and electrical properties of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$. Part I. The system $La_{0.8}Sr_{0.2}Co_{1-y}Fe_yO_3$. *Solid State Ionics*, 1995, **76**, 271–295.
10. Kuščer, D., Holc, J., Hrovat, M., Bernik, S. and Kolar, D., Electrical and microstructural characteristics of materials in the $LaFeO_3$–$LaAlO_3$–$SrFeO_{3-\delta}$ system. In *Proceedings 5th Int. Symp. on SOFC*, ed. U. Stimming, S. C. Singal, T. Tagawa and W. Lehnert. The Electrochemical Society, Aachen, 1997, pp. 947–955.
11. Roth, R. S. and Cook, L. P., *Phase Diagrams for Ceramists*, ed. G. Smith. Vol. IV. 1981, The American Ceramics Society, Fig. 5232, p. 133.
12. Levin, E. M., Robbins, C. R. and McMurdie, H. F., *Phase Diagrams for Ceramists*. ed. M. K.Reser. Vol. II. 1969. The American Ceramics Society, Fig. 2178, p. 45.
13. Levin, E. M. and McMurdie, H. F., *Phase Diagrams for Ceramists*. ed. M. K.Reser. Vol. III. 1975. The American Ceramics Society, Fig. 4377, p. 135.
14. Levin, E. M. and McMurdie, H. F., *Phase Diagrams for Ceramists*. ed. M. K.Reser. Vol. III. 1975, The American Ceramics Society, Fig. 4361, p. 128.