Journal of Alloys and Compounds 480 (2009) 958–961

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of Ca^{2+} and Zn^{2+} cations substitution on the properties of $La_{0.85}Sr_{0.15}CrO_3$ as SOFC interconnect

Xiaofang Zhu, Haitao Gu, Han Chen, Yifeng Zheng, Lucun Guo*

College of Materials Science and Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing 210009, People's Republic of China

ARTICLE INFO

Article history:
Received 4 January 2009
Received in revised form 18 February 2009
Accepted 21 February 2009
Available online 5 March 2009

Keywords:
SOFC
Interconnect
Sinterability
TEC
Electrical conductivity

ABSTRACT

The effect of Ca^{2+} and Zn^{2+} cations substitution on the sinterability, thermal expansion and electrical properties of $La_{0.85}Sr_{0.15-x}Ca_xCr_{1-y}Zn_yO_3$ as solid oxide fuel cell (SOFC) interconnect materials was investigated. The results showed that the bulk densities of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ increased with increasing Ca content and a maximum electrical conductivity value of 20.1 S/cm at 800 °C was obtained when $x = 0.05$. The transition metal Zn substituted in Cr-site further optimized the sinterability and increased the bulk density by 25% when Zn content was up to 0.09. The $La_{0.85}Sr_{0.1}Ca_{0.05}Cr_{0.91}Zn_{0.09}O_3$ sample exhibited an electrical conductivity of 21.5 S/cm at 800 °C and a thermal expansion coefficient (TEC) of 10.3×10^{-6} K^{-1} (20–800 °C), which is compatible with that of 8 mol.%-Y_2O_3-stabilized-ZrO_2 (8YSZ) electrolyte.

1. Introduction

The solid oxide fuel cell (SOFC) is a promising new supply of clean efficient energy for electrical power generation. The interconnect is one of the most important components for SOFC stacks. Alkaline earth metal (AE = Mg, Ca and Sr)-doped lanthanum chromite ($LaCrO_3$) perovskites are considered as candidates for interconnect materials in high-temperature SOFCs owing to their thermal, chemical stability and high electrical conductivity at both reducing and oxidizing atmospheres [1–3]. However, it is well known that these perovskite materials have some problems, such as poor sinterability in air resulting from the volatilization of chromium, an unmatched thermal expansion coefficient (TEC) with that of other components of the SOFC and insufficiently high conductivity [4]. In order to apply the lanthanum chromites to the SOFC interconnects, many investigations have been conducted to improve the properties of the perovskites by doping alkaline metals or transitional metals at La-site or Cr-site. Ding et al. [5] have reported that $La_{0.85}Sr_{0.15}CrO_3$ showed linear thermal expansion behavior and its TEC value was very close to that of 8 mol.%-Y_2O_3-stabilized-ZrO_2 (8YSZ) electrolyte, while it suffered from poor sinterability in air. Kim et al. [6] have found that the $(La_{1-x}Sr_x)CrO_3$ must be sintered at relative high temperatures and that the $(La_{1-x}Ca_x)CrO_3$ perovskite showed better sinterability and solubility in comparison with the phase $(La_{1-x}Sr_x)CrO_3$, but the lower chemical stability with the different components of the SOFC. Partial substitution of Sr atoms by Ca in $(La_{1-x}Sr_x)CrO_3$ was effective in lowering SrO activity and improving sinterability of the perovskite. It has been reported that the double doping of strontium and zinc greatly enhanced the densification of $LaCrO_3$, whereas the effect of doping on the electrical conductivity behavior was not reported [7]. Few studies on the effect of co-doping on A-site have been reported.

In this study, the investigation on the effect of Ca^{2+} and Zn^{2+} cations substitution on sinterability, crystal structure, thermal expansion and electrical conductivity properties of $La_{0.85}Sr_{0.15}CrO_3$ was performed.

2. Experimental procedure

AE- or/and ME-doped lanthanum chromites were prepared using conventional ceramic methods. As starting material powders, La_2O_3 (99.9%), $SrCO_3$ (99.7%), $CaCO_3$ (98%), ZnO (99%), Cr_2O_3 (99%) were used. These powders were thoroughly mixed with distilled water for 8 h, using zirconia milling media in a planetary mill. After drying, the mixtures were ground and then calcined at 1000 °C in air for 2 h. The as-synthesized powders were milled again with distilled water for 6 h. After drying, the powders with 5 wt.% PVA solution were die-pressed into pellets of 20 mm in diameter under pressure of 100 MPa for the density measurement. Bars of 62 mm × 5 mm × 5 mm were also pressed at 100 MPa for thermal expansion and conductivity test.

Various sintered samples were identified by X-ray diffraction analysis on the ARL X'TRA diffractometer using Cu Kα radiation. The bulk densities of the sintered pellets were measured by Archimedes method. TECs were measured using an RPZ-01P dilatometer from room temperature to 800 °C with a heating rate of 5 °C/min. The electrical conductivity of sintered rectangular bars was measured using DC four-terminal method. The sintered bars with Ag paste were fired at 600 °C for 30 min. Four Pt leads were attached to the samples

---

* Corresponding author. Tel.: +86 25 83587261; fax: +86 25 83306152.
E-mail address: lc-guo@163.com (L. Guo).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.02.095

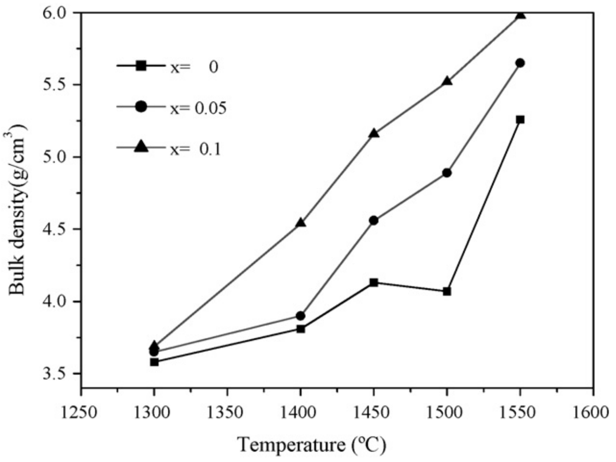

Fig. 1. Bulk density of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ as a function of sintering temperature.

to measure conductivities from 100 °C to 800 °C in air with a heating rate of 5 °C/min.

3. Results and discussion

3.1. *Effect of Ca^{2+} substitution on A-site of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$*

Fig. 1 shows the effect of sintering temperature and calcium dopant concentration on the sinterability of $La_{0.85}Sr_{0.15}CrO_3$. It can be found that the densities of the sintered bodies increased with sintering temperature. The densification of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ was studied for values of $x = 0$, 0.05 and 0.1 as a function of temperatures. The substitution of Ca for Sr in $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ enhanced the sinterability over $La_{0.85}Sr_{0.15}CrO_3$ sample, which is consistent with that of Kim et al. [6]. They suggested that partial replacement of Sr atoms by Ca might lower SrO activity. However, the formation of the second phase (CaO or La_2O_3) is found to depress the vaporization of the chromium component from $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$, which in turn may facilitate the sintering process [8].

Fig. 2 shows the XRD patterns of the $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ samples sintered at 1450 °C for 3 h. All samples showed pure perovskites phase with orthorhombic symmetry and no other phase was observed.

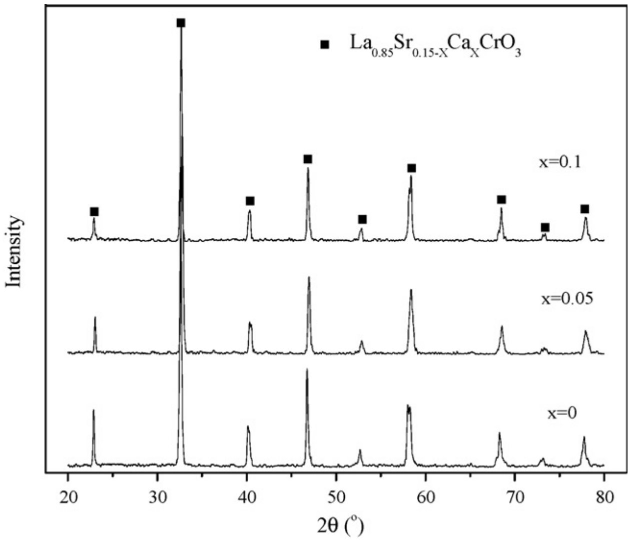

Fig. 2. XRD phase analysis of sintered powers at 1450 °C for 3 h.

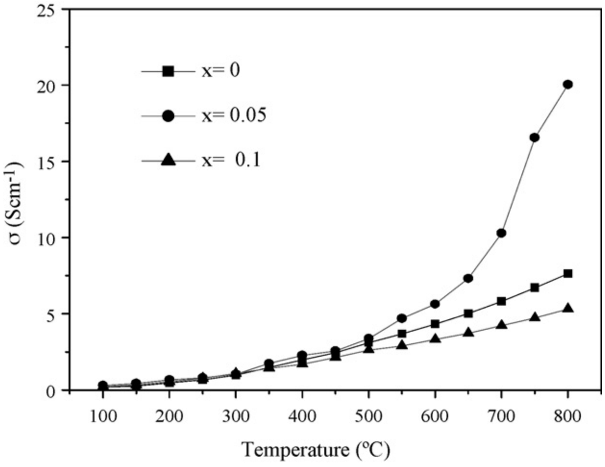

Fig. 3. The electrical conductivity of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ as a function of temperature.

Fig. 3 shows the electrical conductivity of $La_{0.85}Sr_{0.15-x}Ca_xCrO_3$ samples sintered at 1550 °C for 3 h in the temperature range from 100 °C to 800 °C. Because pure $LaCrO_3$ is a p-type conductor, doping with lower valency AE for La^{3+} results in a charge compensating transition of Cr^{3+} to Cr^{4+} ions, which obeys the small polaron hopping mechanism [9]. Accordingly, its electrical conductivity increased with temperature. In addition, it can be found the electrical conductivity increased dramatically with increasing Ca content up to 0.05, and then decreased. The electrical conductivity reached a highest value of 20.1 S/cm when Ca content was 0.05. This is postulated as being due to the enhanced densification that promoted the electrical conductivity. Above the critical dopant content, the charge carrier mobility plays a dominant role. However, higher doping level leads to more lattice distortion which may hinder the transportation of electrical holes. It is likely that greater lattice distortion will lead to less charge carrier mobility, and subsequently lower electrical conductivity [2].

Based on the above results, $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ was chosen as the base material for the study of B-site doping in order to lower the sintering temperature.

3.2. *Effect of Zn^{2+} substitution on B-site of $La_{0.85}Sr_{0.1}Ca_{0.05}Cr_{1-y}Zn_yO$*

Fig. 4(a) shows the shrinkage of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples as a function of Zn content after heating at 1450 °C for 3 h in air. The substitution of Zn for Cr in $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ caused an increase in the shrinkage of the samples. For example, the substitution of 0.01Zn, for Cr in $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ increased its shrinkage from 10% to 15% and the shrinkage increased with increasing Zn content.

As shown in Fig. 4(b), the bulk density of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples has a similar type of behavior. Obviously, Zn-doped samples showed better sinterability in comparison with that of the $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ sample (the broken line). It was also found that the density increased with increasing Zn content and that the $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{0.91}Zn_{0.09}O_3$ sample exhibited the highest density of 6 g/cm^3. It was thought that Zn and Ca ions might react with the chromite to form a phase with a lower melting point that facilitates densification [10].

Fig. 5 shows TEC of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples as a function of Zn content in the temperature range from 50 °C to 800 °C in air. The broken line represents the TEC of 8 mol.%-Y_2O_3-stabilized-ZrO_2 (8YSZ) electrolyte, which is $\sim 10.3 \times 10^{-6}\,°C^{-1}$ in the temperature range from 50 °C to 1000 °C in air or a H_2 atmosphere

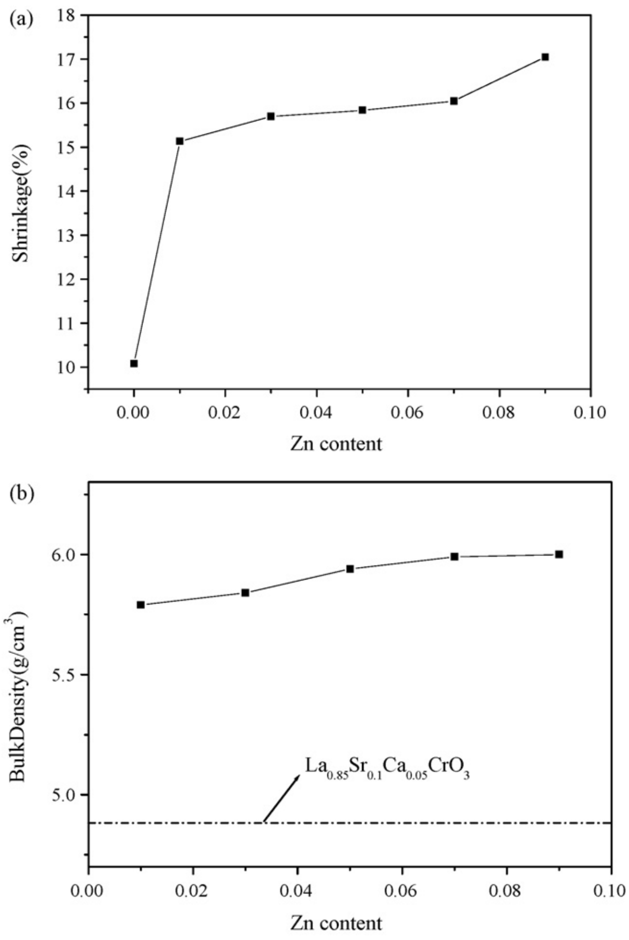

Fig. 4. The sinterability of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ as a function of Zn content.

[11]. Compared with the sample undoped Zn, a slight decrease of TEC was observed for the samples doped Zn, which is attributed to strong interaction to the oxygen sublattice caused by the difference in the radius between Cr and Zn ions [12]. Meanwhile, the TECs of all the samples were very close to that of 8YSZ and had a tendency to increase with increasing Zn content from 0.05 to 0.09. This is associated with the oxygen defect formation. Higher doping level leads to the generation of more oxygen vacancies, which results in larger TECs [2].

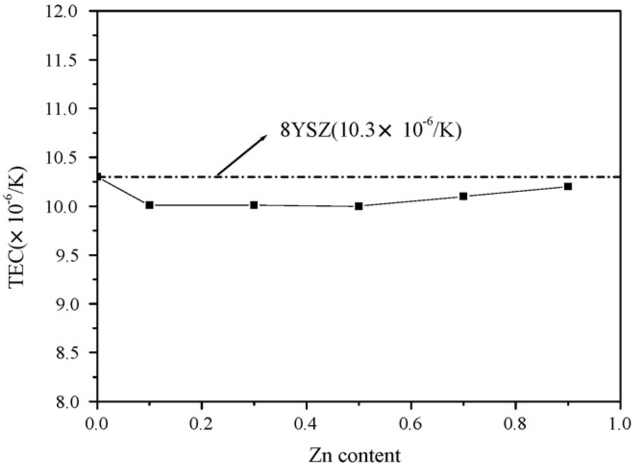

Fig. 5. TEC of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ as a function of Zn content.

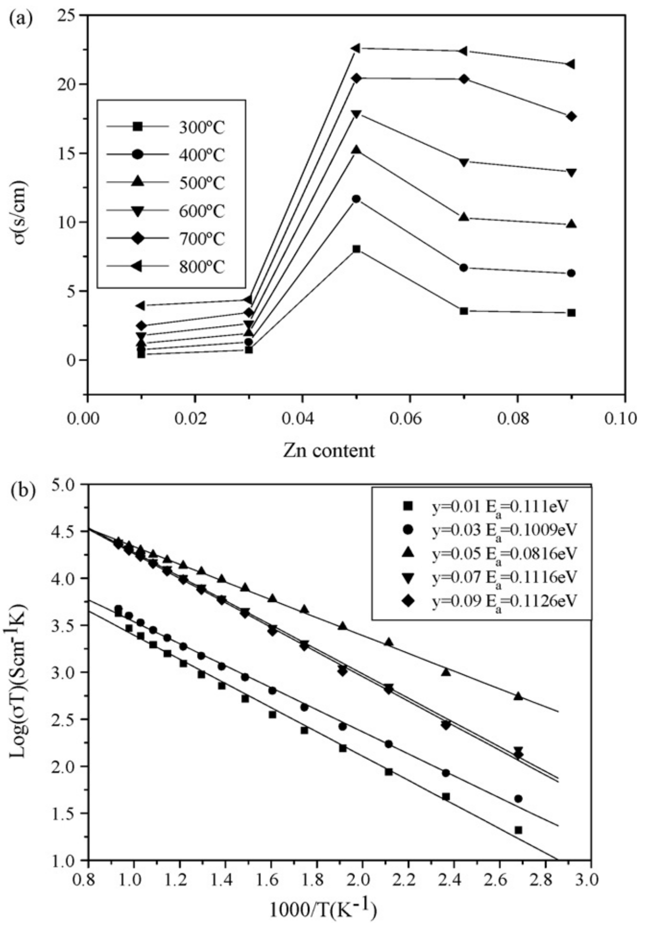

Fig. 6. The electrical conductivity of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples.

Fig. 6(a) shows the electrical conductivity of $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples with different Zn contents in air. The conductivity of the samples with a specific Zn content increased with increasing temperature. It is well known that the electrical transport in doped $LaCrO_3$ is dominated by small-polaron hopping of charge carrier localized at the Cr-site in an oxidizing atmosphere [2]. In addition, Fig. 6(a) showed that increasing Zn concentration caused considerable increase in electrical conductivity. Increasing dopant content enhances the electron hole concentration thus promoting the electrical conductivity. This can be understood as a result of enhanced electron hole concentration via electronic compensation mechanism [2]. When $y \geq 0.05$, the conductivity of the samples doped Zn at 800 °C was higher compared with the $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ sample, and in particular, the sample containing 0.05Zn showed the highest conductivity and reached as high as 22.5 S/cm at 800 °C.

The relationship between the electrical conductivity and the temperature, is established to obey the following equation, which is typical of p-type conductor behavior:

$$\sigma = \left(\frac{A}{T}\right) \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where A is a pre-exponential factor, k the Boltzmann constant, T the absolute temperature and E_a the activation energy for the conduction [13]. As shown in Fig. 6(b), all samples exhibited linear conductivity behavior in the temperature range from 100 °C to 800 °C and a linear plot of $\ln(\sigma T)$ vs $1/T$ was achieved. This is often cited as convincing evidence that thermally activated hopping of small polarons is responsible for the conduction process. The corresponding activation energy decreased from 0.111 eV to 0.0816 eV with the increasing Zn content in $La_{0.85}Sr_{0.15}Ca_{0.05}Cr_{1-y}Zn_yO_3$ samples. With $y > 0.05$, the activation energy increased.

4. Conclusions

The calcium ion was substituted for $La_{0.85}Sr_{0.15}CrO_3$ in La site to investigate its effect on the sinterability and electrical conductivity. The co-doping in A-site effectively enhanced the sinterability and electrical conductivity. The bulk density increased with increasing Ca dopant concentration and the $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ sample showed the highest conductivity of 20.1 S/cm at 800 °C. The additional substitution of zinc ion for Cr can significantly lower the sintering temperature in air. With the increase of Zr content, the bulk density increased, reaching 6.0 g/cm^3 when the Zn content was 0.09. The dense $La_{0.85}Sr_{0.1}Ca_{0.05}C_{r0.91}Zn_{0.09}O_3$ sample exhibited excellent electrical conductivity of 21.5 S/cm at 800 °C, which is as high as that of $La_{0.85}Sr_{0.1}Ca_{0.05}CrO_3$ sample and its TEC value was in good agreement with that of 8YSZ electrolyte.

Acknowledgements

This work was financially supported by the Commercialization of Scientific and Technological Achievements Program of Jiangsu Province (BA2006049). We also acknowledge the support of Jiangsu Province Key Laboratory of Inorganic and Composite Materials.

References

[1] Q. Minh Nguyen, J. Am. Ceram. Soc. 76 (1993) 563–588.
[2] W.Z. Zhu, S.C. Deevi, Mater. Sci. Eng. A348 (2003) 227–243.
[3] J.W. Fergus, Solid State Ionics 171 (2004) 1–15.
[4] X.L. Zhou, J.J. Ma, F.J. Deng, G.Y. Meng, X.Q. Liu, Solid State Ionics 177 (2007) 3461–3466.
[5] X.F. Ding, Y.J. Liu, L. Gao, L.C. Guo, J. Alloys Compd. 425 (2006) 318–322.
[6] J.H. Kim, D.H. Peck, R.H. Song, K. Hilpert, J. Electroceram. 177 (2006) 29–733.
[7] S. Hayashi, K. Fukaya, H. Saito, J. Mater. Sci. Lett. 7 (1988) 457–458.
[8] N.M. Sammes, R. Ratnaraj, J. Mater. Sci. 19 (1994) 4319–4324.
[9] S.P. Simner, J.S. Hardy, J.W. Stevenson, T.R. Armstrong, Solid State Ionics 128 (2000) 53–63.
[10] M. Masashi, N.M. Sammes, Solid State Ionics 146 (2002) 301–312.
[11] H. Hayashia, T. Saitoua, N. Maruyamaa, Solid State Ionics 176 (2005) 613–618.
[12] S. Tanasescu, D. Berger, D. Neiner, N.D. Totir, Solid State Ionics 157 (2003) 365–370.
[13] X.L. Zhou, M.X. Zhu, F.J. Deng, G.Y. Ming, X.Q. Liu, Acta Mater. 55 (2007) 2113–2118.