Solid State Ionics 201 (2011) 35–41

Contents lists available at ScienceDirect

Solid State Ionics

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

Characterization of $Ln_{0.5}M_{0.5}FeO_{3-\delta}$ (Ln = La, Nd, Sm; M = Ba, Sr) perovskites as SOFC cathodes

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ARTICLE INFO

Article history:
Received 5 January 2011
Received in revised form 19 July 2011
Accepted 28 July 2011
Available online 13 September 2011

Keywords:
Cathode
Electrical conductivity
Microstructure
Perovskite structure
SOFC

ABSTRACT

$Ln_{0.5}M_{0.5}FeO_{3-\delta}$ (Ln = La, Nd, Sm; M = Ba, Sr) perovskites have been synthesised by the glycine-nitrate route in order to obtain compounds with good morphological and electrical characteristics to be used as SOFC cathodes. A systematic study of the influence of the average ionic radius of the A cation ($<r_A>$), on the structural, morphological and electrical properties of these perovskites has been performed. The obtained materials have been characterised by ICP-AES analysis, X-ray powder and neutron powder diffraction, scanning electron microscopy and four-probe conductivity measurements. In this study $<r_A>$ has been changed in the range $1.34 \geq <r_A> \geq 1.25$ Å, while keeping constant the doping level, x = 0.5 (in A position) and A cation size disorder, $\sigma^2(r_A) = 0.0161$ Å^2. Overall, the sample with the higher average ionic radius showed the highest values of conductivity. Chemical compatibility of the proposed cathodes with yttria-stabilised zirconia electrolyte (YSZ) has also been analysed. The data indicate that additional phase formations exist in all systems at temperatures above ~1000 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have been for long considered as efficient devices for the direct conversion of the chemical energy of a fuel into electrical power, combining the benefits of environmentally friendly power generation with the advantage of fuel flexibility [1]. Conventional SOFCs use to operate at high temperatures (800–1000 °C) to maximise fuel conversion but this is also the origin of several long term problems, such as the interfacial reaction between the cathode and the electrolyte, and the degradation of the anode via particle coarsening. The use of intermediate temperatures (IT, 600–800 °C) is expected to overcome some of these problems but the decrease of the performance associated with a low operation temperature is still a concern, mainly with respect to the cathode [2]. The development of new cathode materials for these temperatures is thus an active field of research. Materials with the perovskite structure (ABO_3) are the most widely studied as IT-SOFC cathodes due to the ability of this structure to tolerate extensive modifications in its composition [3]. It has been demonstrated that the appropriate selection of the A- and B-site elements (or element combinations) can change their electrical and electrochemical characteristics and thus render them more useful as SOFC cathodes [4,5].

The A position is usually occupied by a mixture of rare and alkaline earths cations (Ln^{3+}: La, Sm, Nd, Pr and/or M^{2+}: Sr, Ba, Ca) and the B site by a first-row transition metal (Mn, Fe, Co) or a mixture of them [6]. Among the most studied IT-SOFC cathodes, the mixed ionic and electronic conductors $La_{1-x}Sr_xFeO_3$, $La_{1-x}Sr_xCoO_3$ or $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ are worth mentioning [7–9]. Of these, iron based perovskites have shown low reactivity with the standard electrolyte, ytria-stabilised zirconia (YSZ), together with a good thermal expansion coefficient (TEC) matching [10,11]. Both are required characteristics for a cathode in order to avoid the side formation of unwanted and poor conducting phases in the cathode-electrolyte interphase during fabrication and operation, and also to prevent mechanical stresses that could destroy this interphase.

Compounds with the general formula $La_{1-x}A_xFeO_3$ have shown their highest electrical conductivity and the best cathode performances with intermediate x compositions (or doping levels) [12–14] but are also highly dependent on other structural factors such as the tolerance factor (t) and the mean A site-radii ($\langle r_A \rangle$) [15–18]. Moreover, it has for long been demonstrated that even the disorder of Ln^{3+} and M^{2+} cations with different sizes distributed over the A site have important implications in the properties of these type of perovskites [19]. To quantify this effect, the variance of the A-cation radius distribution, $\sigma^2(r_A)$, is used: for two or more A-site species with fractional occupancies yi ($\sum yi = 1$), the variance of the ionic radii r_i about the mean $<r_A>$ is:

$$\sigma^2(r_A) = \sum y_i r_i^2 - \langle r_A \rangle^2. \quad (1)$$

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doi:10.1016/j.ssi.2011.07.019

Table 1
Series of $Ln_{0.5}M_{0.5}FeO_3$ (Ln = La, Nd, Sm; M = Ba, Sr) perovskites.

$Ln_{0.5}M_{0.5}FeO_{3-\delta}$	$<r_A>$ (Å)	$\sigma^2(r_A)$ (Å^2)	t
$La_{0.5}Ba_{0.5}FeO_{3-\delta}$	1.34	0.0161	1.02
$La_{0.34}Nd_{0.16}Sr_{0.12}Ba_{0.38}FeO_{3-\delta}$	1.31	0.0161	1.00
$La_{0.04}Nd_{0.46}Sr_{0.24}Ba_{0.26}FeO_{3-\delta}$	1.28	0.0161	0.99
$La_{0.05}Sm_{0.45}Sr_{0.32}Ba_{0.18}FeO_{3-\delta}$	1.25	0.0161	0.98

Table 2
Summary ICP results for $Ln_{0.5}M_{0.5}FeO_{3-\delta}$ (Ln = La, Nd, Sm; M = Ba, Sr) perovskites.

Nominal composition	Elemental composition				
	La	Nd/Sm	Ba	Sr	Fe
$La_{0.5}Ba_{0.5}FeO_{3-\delta}$	0.48(1)		0.49(1)		1.00(1)
$La_{0.34}Nd_{0.16}Sr_{0.12}Ba_{0.38}FeO_{3-\delta}$	0.34(1)	0.16(1)	0.39(1)	0.12(1)	1.00(1)
$La_{0.04}Nd_{0.46}Sr_{0.24}Ba_{0.26}FeO_{3-\delta}$	0.04(1)	0.45(1)	0.24(1)	0.26(1)	1.00(1)
$La_{0.05}Sm_{0.45}Sr_{0.32}Ba_{0.18}FeO_{3-\delta}$	0.05(1)	0.44(1)	0.31(1)	0.18(1)	1.00(1)

Previous studies in similar perovskite oxides showed good cathode performances for those compounds with high average ionic radius of A-site cations and low A cation size disorder [20,21].

The aim of this work is the evaluation of the effect of the variation of $<r_A>$ on the properties of four different phases proposed as possible SOFC cathodes, $Ln_{0.5}M_{0.5}FeO_{3-\delta}$ (Ln = La, Nd, Sm; M = Ba, Sr). These properties include crystal structure, morphology and electrical conductivity. A comparative study on the reactivity of these compounds with YSZ was also performed. For this series (Table 1), $<r_A>$ has been varied between 1.34 and 1.25 Å keeping x and $\sigma^2(r_A)$ constant, with values of 0.5 and 0.0161 Å^2, respectively.

Given that together with the structural considerations the morphological characteristics of the perovskite powders are also a key factor to be optimised for an appropriate SOFC cathode [22,23], we have also looked into an optimum synthetic method. Among the different synthetic routes, the glycine-nitrate method has been cited as a suited technique for preparing this type of perovskite cathodes as compared to traditional synthetic methods such as the ceramic route [24,25]. The main advantage of the process is that it leads to powders with large compositional homogeneity and nanometric particle sizes. Consequently, this is the method that we have chosen for the present study.

2. Experimental

All $Ln_{0.5}M_{0.5}FeO_{3-\delta}$ (Ln = La, Nd, Sm; M = Ba, Sr) perovskites (Table 1) were synthesised by the glycine-nitrate route under identical conditions. The aqueous metal-nitrate solutions were mixed with constant stirring on a hot plate. These solutions were heated to evaporate the excess of water and, afterwards, the glycine was added. A glycine/nitrate molar ratio of 2:1 was used. The mixture results in a viscous liquid which was ignited by quickly heating the solutions to approximately 400 °C.

The obtained powders were pelletized and calcined at 800 °C for 2 h to remove carbon residues. To obtain the final materials, these powders were again pelletized and calcined, with intermediate grindings, at 850, 950 and 1050 °C. In each step, samples were kept for 10 h at the highest temperature and the process was always carried out under air.

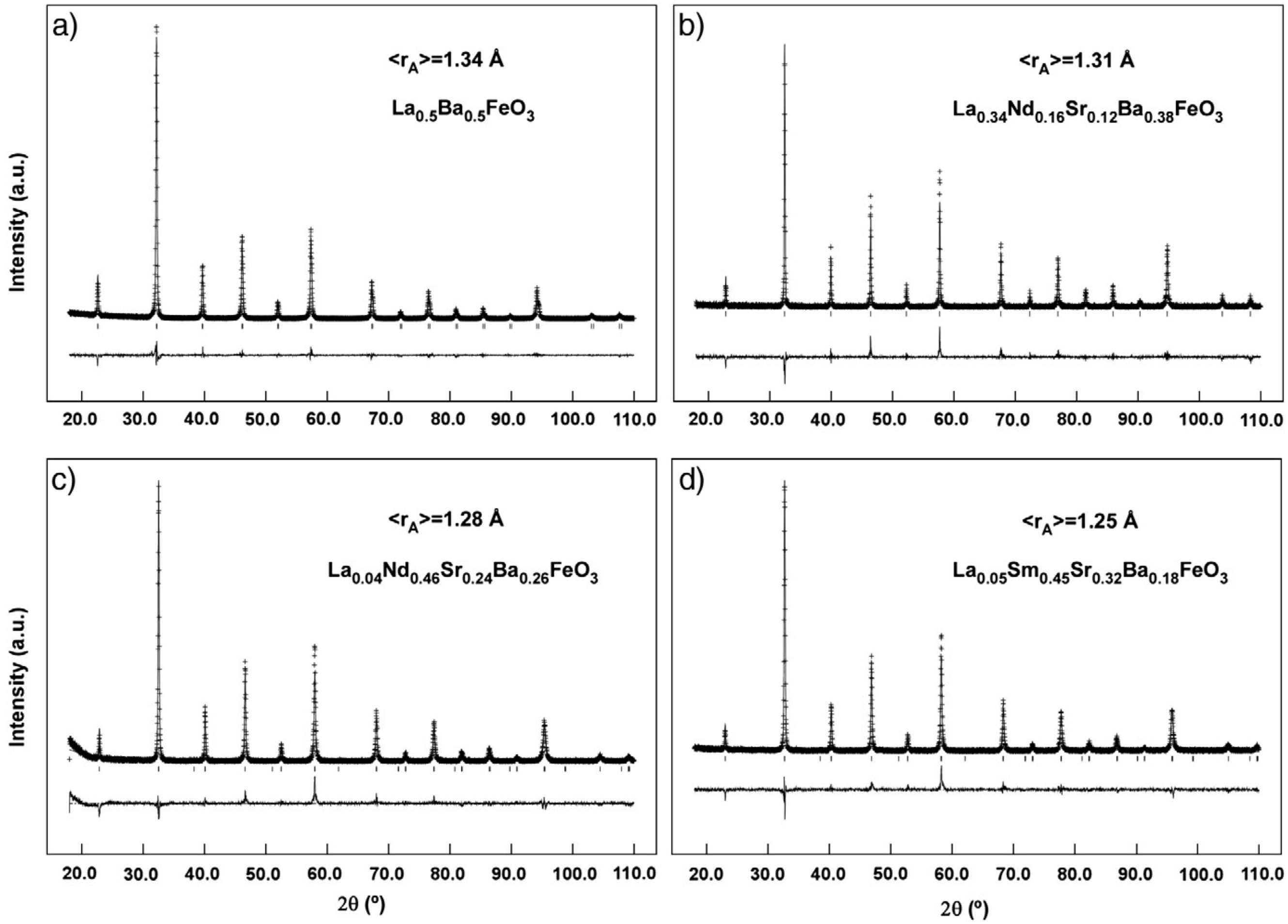

Fig. 1. Rietveld fits to the X-ray powder diffraction patterns at room temperature for (a) $<r_A>$ = 1.34 Å, (b) 1.31 Å, (c) 1.28 Å and (d) 1.25 Å samples.