ARTICLE IN PRESS
SOSI-14251; No of Pages 6

Solid State Ionics xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

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

Oxygen isotope exchange, water uptake and electrical conductivity of Ca-doped lanthanum zirconate

E.P. Antonova [a,b,*], A.S. Farlenkov [a,b], E.S. Tropin [a,b], V.A. Eremin [a,b], A.V. Khodimchuk [a,b], M.V. Ananyev [a,b]

[a] *Institute of High Temperature Electrochemistry UB RAS, Akademicheskaya str. 20, Yekaterinburg 620137, Russia*
[b] *Ural Federal University, Mira av. 19, Yekaterinburg 620002, Russia*

ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form 17 February 2017
Accepted 24 March 2017
Available online xxxx

Keywords:
Water uptake
Oxygen diffusion
Proton conduction

ABSTRACT

Proton concentration of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ in H_2O–O_2 atmospheres has been measured by means of the method of high temperature thermogravimetry. The oxygen diffusion coefficient and the oxygen surface exchange coefficient have been measured for $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ over the temperature range of 600–900 °C using the oxygen isotope exchange method with gas phase equilibration. pO_2-dependencies of the electrical conductivity have been determined in the temperature range 500–800 °C and oxygen partial pressure range of $10^{-20} < pO_2 < 0.21$ atm in atmosphere saturated with water vapour at 25 °C ($pH_2O = 0.03$ atm). Ionic conductivity has been divided into protonic and oxygen-ionic components. The influence of oxygen defect structure on the water uptake, oxygen diffusivity and electrical conductivity of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ has been discussed.

1. Introduction

Discovery of high-temperature proton conduction in solid oxides causes many attempts to find new materials with high proton conductivity. The use of these materials in solid oxide fuel cells (SOFCs) has a number of advantages over conventional oxygen-ionic conductors such as reduced working temperatures and elimination of fuel dilution with water vapour. The most well-known and studied high temperature proton conductors have a perovskite structure [1]. Recently it was reported that doped $La_2Zr_2O_7$ with a pyrochlore-type structure (space group $Fd\overline{3}m$ can exhibit high-temperature proton conductivity [2–7]. These materials are of great interest because of the presence of intrinsic oxygen vacancies on the *8b* sites in their structure and as a consequence the presence of intrinsic oxygen-ionic conductivity.

There are several papers regarding the theoretical studies of conduction mechanisms in these oxides [2,3] and their electrical properties [4,5]. Some researchers have made attempts to clarify the relationship between the electrical conductivity and disordering of oxide-ion sublattice in pyrochlore structure. For example, Hagiwara et al. [6] found that the oxygen-ionic conductivity increased with the increase of the oxygen *8b* site occupancy. However, the complete understanding of the conduction mechanisms in these materials is not achieved yet. There is a lack of data concerning with the water uptake and surface exchange kinetics in the oxides. This study focuses on the investigation of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ in order to reveal the peculiarities of oxygen isotope exchange, water uptake and ionic transport in the oxide depending on external conditions.

2. Experimental

2.1. Samples preparation

Powders of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ were prepared by a citric-nitrate technology, all reagents ($Zr(CO_3)_2$, La_2O_3, $CaCO_3$) were of a high purity grade. $La(NO_3)_3$, $Zr(NO_3)_4$ and $Ca(NO_3)_2$ solutions were prepared and mixed in stoichiometric ratios. Concentrations of the main elements were controlled by the atomic emission spectroscopy applying OPTIMA 4300 DV (Perkin Elmer, USA) spectrometer. After that water solution of citric acid was introduced into a nitrate mixture, the amount of acid corresponded to the total number of moles of metal cations. The resulting solution was kept at 70 °C during 16 h while stirring with a magnetic stirrer. The remaining moisture was evaporated to form a powder. The powder was annealed in ambient air at the temperature of 1000°C during 2 h with the subsequent grinding. Final annealing was performed at 1350°C during 4 h. Obtained powders were compacted in tablets by isostatic pressing ($P = 30$ tons) with the subsequent sintering in ambient air at the temperature of 1600°C during 5 h.

2.2. Samples characterization

The X-ray powder diffraction (XRD) and structural analysis were carried out by using D/MAX-2200 RIGAKU conventional diffractometer in $Cu_{K\alpha}$-radiation ($\lambda(K_{\alpha 1}) = 1.54$ Å) at room temperature in ambient air. Structural Rietveld refinement of X-Ray powder patterns was

---

* Corresponding author at: Institute of High Temperature Electrochemistry UB RAS, Akademicheskaya str. 20, Yekaterinburg 620137, Russia.
E-mail address: antonova_ek@list.ru (E.P. Antonova).

http://dx.doi.org/10.1016/j.ssi.2017.03.023
0167-2738/© 2017 Elsevier B.V. All rights reserved.

Please cite this article as: E.P. Antonova, et al., Oxygen isotope exchange, water uptake and electrical conductivity of Ca-doped lanthanum zirconate, Solid State Ionics (2017), http://dx.doi.org/10.1016/j.ssi.2017.03.023

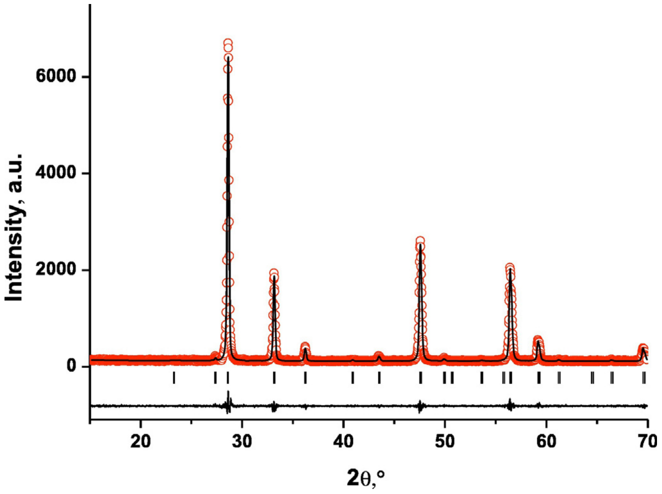

Fig. 1. XRD pattern for $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ with the Rietveld refinement: circles – experimental data, lines – fitting and residual, dash points – Bragg's positions of peaks.

carried out by FullProf computer program [8]. All the diffraction peaks of the $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ could be indexed as a pyrochlore structure (see Fig. 1), space group $Fd\overline{3}m$ (lattice parameter $a = 1.0811(4)$ nm). The Rietveld refinement of the XRD data confirms the phase purity of the sample. There are four possible choices of origin in this space group; the most commonly used places the smaller B-type cation at the *16c (0, 0, 0)* site and the larger A-type cation at *16d (1/2, 1/2, 1/2)*. There are two occupied anion sites, with O at *48f (x, 1/8, 1/8)*, and O′ at *8b (3/8, 3/8, 3/8)*. In this structure the cubic lattice parameter, a, and the positional parameter, x, for the O atom in *48f* are the only structural variables [9]. In our study the case of the setting centred in *-43m* was considered, the site called *8a (0, 0, 0)* was occupied while the site *8b (1/2, 1/2, 1/2)* was vacant.

Particle size distribution of the samples was analyzed by the laser scattering method using Malvern Mastersizer 2000 (Malvern Instruments, United Kingdom). It can be seen (Fig. 2) that there are two peaks in the particle size distribution function at 5 and 30 μm.

The specific surface area of the samples was determined by BET method using Sorbi N.4.1 (Meta, Russia). Prior to the measurements, the samples were degassed for 1 h with flowing ultrahigh-purity helium (99.995% purity) at the temperature of 200 °C. The specific surface area value was found to be 1.35 ± 0.01 m^2/g.

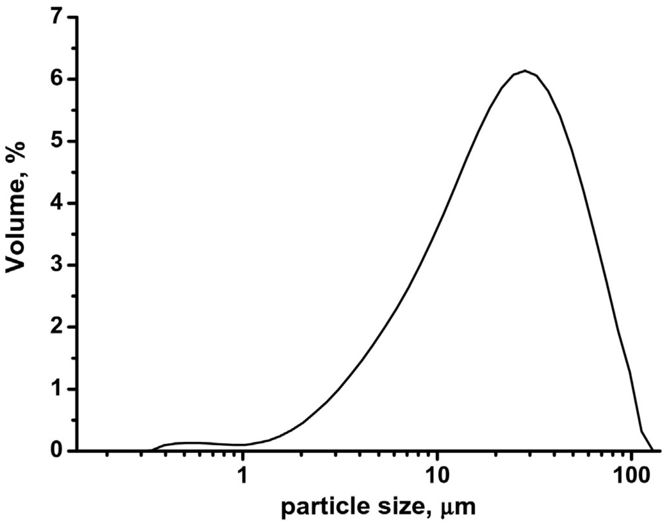

Fig. 2. Particle size distribution function of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ powdered sample.

2.3. Water uptake measurements

Thermogravimetric analysis (TGA) was performed using simultaneous thermal analyzer STA Jupiter 449 F1 (Netzsch, Germany) with water vapour generator Asteam DV2MK (Adrop, Germany). The as-prepared powders were heated up to 950 °C and held at this temperature for 8 h under the mixture of dry argon (99.998% purity) and dry oxygen (99.999% purity) to release water from the crystal structure. After that the carrier gas was saturated with water ($pH_2O = 0.24$ atm, $pO_2 = 0.18$ atm) and then the increase of weight was recorded upon cooling from 950 to 300 °C with the cooling rate of 60 °C/h with a 2 and 5 h stabilization time at 950 and 300 °C, respectively. Before the thermogravimetric measurements, each sample was dried in high vacuum with the residual pressure of 10^{-9} atm in vacuum at 950 °C for 1 h with a heating rate of 60 °C/h. This procedure was necessary in order to achieve the initial reproducible state for each sample.

The method of Temperature-Programmed Desorption (TPD) with Mass-Spectrometric (MS) analysis was used to determine the composition of the gases desorbed from the specimens. The experiments were done using vacuum experimental rig with quadrupole mass-spectrometer (Microvion2, MKS Instruments, UK). Before the TPD-measurements the system was pumping down with the residual pressure of 10^{-9} atm at 950 °C for 1 h with a heating rate of 60 °C/h. The powders were heated up to 950 °C with the heating rate of 60 °C/h and held at this temperature for 1 h under mass-spectrometer continuous recording of evolved gas composition.

2.4. Oxygen exchange kinetics study

The oxygen surface exchange kinetics was studied on a dense specimen of $La_{1.9}Ca_{0.1}Zr_2O_{7-\alpha}$ using the isotope exchange method with gas phase equilibration (GPE) by means of static circulation setup in the temperature range of 600–900°C at the oxygen pressure of 0.01 atm. The gaseous oxygen of natural isotope composition as well as 89% enriched by ^{18}O-isotope oxygen with the purity of 99.9996% were used for the isotope exchange experiment. The scheme of the experimental rig, the experiment technique and the data treatment details are thoroughly described elsewhere [10–14]. The oxygen surface exchange coefficient (k) and oxygen tracer diffusion coefficient (D) were calculated according to the model derived by Klier et al. [15]. This model is based on simultaneous solution of diffusion and surface exchange equations with the proper boundary and initial conditions:

$$\begin{cases} \frac{N}{S}\dot{\alpha} = r_H(\alpha_S - \alpha) \\ \frac{N}{S}\dot{y} = -ry + 2r_2(\alpha_S - \alpha)^2 \\ \dot{\alpha} = D_O\nabla^2\alpha \\ r = r_0 + r_1 + r_2 \end{cases} \tag{1}$$

where r_H – the heterogeneous exchange rate, S – the surface area of sample; N – the amount of oxygen atoms in the gas phase, α – fraction of ^{18}O isotope in the bulk, α_s –fraction of ^{18}O isotope at the surface, y – difference between the concentration of $^{18}O^{16}O$ molecules fraction at time t and the equilibrium $^{18}O^{16}O$ molecules fraction, D_O – oxygen diffusion coefficient; r_0, r_1 and r_2 – the rates of three exchange types. Indexes 0, 1 and 2 show the amount of oxygen from the solid surface interacting in a single exchange act; r – is the sum of the rates of three exchange types.

The oxygen surface exchange coefficient is related to the oxygen heterogeneous exchange rate according to the following equation:

$$k = r_H \frac{M_r}{\left(3 - \frac{x}{2}\right) N_a \rho} \tag{2}$$

Please cite this article as: E.P. Antonova, et al., Oxygen isotope exchange, water uptake and electrical conductivity of Ca-doped lanthanum zirconate, Solid State Ionics (2017), http://dx.doi.org/10.1016/j.ssi.2017.03.023