



Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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



Feature article

Structural modifications of lanthanum silicate oxyapatite exposed to high water pressure

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ARTICLE INFO

Article history:

Received 16 November 2016

Received in revised form

16 December 2016

Accepted 20 December 2016

Available online xxx

Keywords:

Oxyapatite

Powders solid-state reaction

PCFC

Protonation

Structure

ABSTRACT

Dense lanthanum silicate oxyapatite samples $\text{La}_{9.33+x}(\text{SiO}_4)_6\text{O}_{2+3x/2}$ were exposed to high water pressure in autoclave, in order to study the effects of oxygen stoichiometry and treatment duration on the protonation of these materials. TG analyses showed that protonic species were successfully introduced into the bulk of the material, especially for $\text{La}_{9.60}(\text{SiO}_4)_6\text{O}_{2.4}$ sample after 84 h of treatment at 550 °C under 40 bar water pressure. It was shown that the mass loss compares well with perovskite materials and increases when protonation time rises (0.66% above 600 °C for 408 h), with a time limit beyond which the microstructure is no more stable.

Rietveld refinement and Raman spectroscopy studies confirmed some structural modifications which could be linked to the incorporation of protonic species. It was shown that autoclave treatment induced an increase of the cell volume related to an increase of the a and b lattice parameters (enlargement of the characteristic channels of oxyapatite).

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1. Introduction

The development of environment-friendly electrochemical applications and clean energy conversion systems, such as Solid Oxide Fuel Cells (SOFC), is nowadays attracting a great scientific interest [1,2]. The most common material used as solid electrolyte in SOFC is oxide ion conducting yttria-stabilized zirconia (YSZ) [2,3]. However, current research aims to decrease the working temperature of SOFC down to intermediate temperatures (600–800 °C) by using new oxide ion conductors with equivalent conductivity values than YSZ at 1000 °C (above 0.1 S cm^{-1}). Apatite-type lanthanum silicates of general formula $\text{La}_{9.33+x}(\text{SiO}_4)_6\text{O}_{2+3x/2}$, found by Nakayama et al. [4,5], are one of the most promising oxide ion conductors for application as electrolyte in Intermediate-Temperature SOFC (IT-SOFC) [5–9]. Their structure is based on a 3-dimensional organization of isolated silica tetrahedral and forms large lanthanum oxide tunnels oriented along the c-axis

[10–12]. Such a structure can explain that oxyapatites exhibit high anisotropic conductivity in the c direction, which is increased by the incorporation of interstitial oxygen inside the large tunnels (formula with $x > 0$) [6–9,13–15]. The reactive diffusion method reported by Fukuda et al. [6,7,11,16] allows the elaboration of highly c-axis oriented lanthanum silicate apatite polycrystal material which exhibited high oxide ion conductivity values: $2.4 \times 10^{-3} \text{ S cm}^{-1}$ to $2.39 \times 10^{-2} \text{ S cm}^{-1}$ from 573 to 973 K with an activation energy of 0.35 eV (in agreement with the calculated migration energy of 0.32 eV linked to an original push-pull mechanism [14,17]).

Recent studies [18–20] show that the apatite structure could also enable the incorporation and conduction of protons. Thus, oxyapatite might be a new promising proton-conducting material for application as electrolyte in Proton Conducting SOFC (PC-SOFC) [21,22], which has the advantage of operating at lower temperatures (400–600 °C). Contrary to anionic conduction, in the case of protonic conduction, the electrolyte material requires a moisturizing step, in order to enable the insertion and conduction of protons, which are not usually present in the material structure. The first works about the protonation of oxides, on the 1950s,

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has been performed on the reduction of ZnO materials which have shown the incorporation of protons in the oxide lattice [23]. Most studies, especially about (Ba, Sr)(Zr, Ce, Ti, Y)O_{3-δ} oxygen deficient perovskite materials [24–30] shows the complexity of water/proton insertion mechanism (called protonation) and the competition between surface and volume protonic species during the protonation step. Colomban et al. [25–28] found out that the pure and dense samples of (Ba, Sr)(Zr, Ce, Ti, Y)O_{3-δ} perovskites, under high pressures of decarbonated water and at high temperature (using an autoclave), promotes the creation of volume protonic species, instead of surface water and surface hydroxycarbonate-type species (which must be avoided in the case of electrolyte materials of PC-SOFC).

Reactions (1a) [31–33] and (1b) [33–36] are the main protonation reactions given in literature to describe the incorporation of water, generally into oxygen-deficient perovskites ceramics.



They lead to a global Reaction (1c) as given by Deng et al. [37]



However, this last assumption is not always confirmed and it is not trivial to determine the nature or position of protons in oxides [24,27,33,38,39]. Also, the dissociation mechanism of water molecules has not yet been well understood in the literature [27].

In the case of apatite material, which can present oxygen interstitials or vacancies, three other protonation reactions can be suggested [19,20] involving oxygen interstitial:



It is possible to evaluate the amount of water dissociated into the host structure of the material by TGA, which is the most common method to measure the proton amount in oxides [25–27,29,40]. For example, in Ba based perovskite system, the total weight loss observed can reveal the departure of free water, chemically bounded water and hydroxides below 600 °C, and the presence of “protonic” species inside the host structure (denoted as bulk “protonic” species) above this temperature. However, the TGA analysis does not allow determining the H content as well as the neutron measurements does [25–27,29]. The variation of mass linked to the protonation or the deprotonation of materials is usually very low (less than 1% in weight). Thus the characterization of protonated materials by TGA method requires starting samples pure and dense, to avoid an overestimation of the mass loss caused by impurities, porosity or specific area of powder (depending on the samples used) [28].

Despite the proton amount in the host structure is often very low, it is usually sufficient to obtain significant proton conduction through the materials (>10⁻³ S/cm) [25,27,30]. For instance, Orera et al. [19] have studied the protonation of a powder of La₈Ba₂(SiO₄)₆O₂ lanthanum silicate at 400 °C for 48 h in a tube furnace under flowing nitrogen bubbled through water at room temperature (pH₂O ≈ 0.03 atm). As this variation of mass was obtained below 400 °C, The low total weight loss of about 0.1% in weight could as well correspond to surface “protonic” species, or dehydration of lanthanum reagent traces and not bulk. In the same way, Corrie et al. [41], had recently reported the protonation of a similar composition of oxyapatite, La_{9,4}(SiO₄)₆O_{2,4}, in a hydrothermal vessel at 200 °C for 48 h. However, the hydration process and TGA analysis reported in this study have also been performed with powder samples. A larger mass loss at 400 °C (about 0.8%wt) than

that previously observed by TGA was observed. A second mass loss between 400 and 500 °C was also measured (about 0.2%wt). These mass losses could be correlated to protonate species incorporated in the lattice structure of apatite at lower temperature than for Ba perovskite systems. Nevertheless, another assumption reported by Corrie et al. is that a part of the mass losses for hydrated apatite samples between 280 °C and 470 °C could be also be attributed to the dehydration of a reagent traces, namely La(OH)₃ (caused by hydrothermal treatment of La₂O₃ residual), complicating all interpretations. Actually, neutron diffraction studies do not allow to localise the proton site, but only a significant increase in the O content between hydrated and dehydrated apatite sample. Corrie et al. assumed that this extra O is charge balanced by protons.

The aim of this paper is the study of the protonation of Si-based oxyapatite La_{9,33+x}(SiO₄)₆O_{2+3x/2} dense ceramic pellets using a high pressure – high temperature autoclave in order to clarify the protonation mechanism in the oxides. This work corresponds to the first study about the eventual protonation of oxyapatite materials with oxygen sub-stoichiometry (x < 0), oxygen-stoichiometry (x = 0) and oxygen over-stoichiometry (x > 0) at high water pressure (40–50 bar). Besides, an aging test was performed on the most promising sample of initial composition La_{9,60}(SiO₄)₆O_{2,4}, in order to study the effect of the duration of the autoclave treatment on the stability and the protonation of the material. Ceramics were characterized by TGA an XRD. Raman spectroscopy was used in order to study the short-range structure according to previous procedure [17,42,43,]. The proton insertion and its distribution/effect in the apatite structure have never been studied using Raman spectroscopy. We discuss here the Raman signature of the large lanthanum oxide channels before and after exposition to high water pressure.

2. Experimental

2.1. Powder synthesis and sintering

Powders of oxyapatite of general formula La_{9,33+x}(SiO₄)₆O_{2+3x/2} (x = -0.2,0,0.27) were synthesized by solid state route from hexagonal La₂O₂CO₃ and SiO₂ reagents as explained in previous work [44,45]. After attrition milling in ethanol for 2 h, the mixture was dried, heated at 1200 °C for 4 h and pressed by isostatic pressing into cylindrical bars at 2000 bar for 1 min. Conventional sintering at 1550 °C for 8 h was used to densify the samples. Finally, the sintered samples were cut using a diamond wire saw in order to obtain dense pellets of 6 mm diameter and 1 mm thickness.

2.2. High water pressure treatments

Ceramic pellets of compositions La_{9,13}(SiO₄)₆O_{1,7} (La913), La_{9,33}(SiO₄)₆O₂ (La933), and La_{9,60}(SiO₄)₆O_{2,4} (La960) were wrapped in gold foil and put in an autoclave with decarbonated water for 84 h at 550 °C and 50 bar. After 12 h of treatment, the pressure had decreased to 40 bar, that could indicate an eventual incorporation of water in the ceramic pellets. A second autoclave treatment was performed in the same initial conditions at 550 °C and 50 bar for 0, 24, 72 and 408 h, on four pellets of composition La960. The notations La913.X, La933.X and La960.X (with X the duration of the high water pressure treatment in hours and “NP” indicating a non protonated sample) will be used in the following sections for the sake of clarity.

2.3. Characterizations

Microstructural observations of the samples were conducted on a JEOL 7400 FEG-SEM scanning electron microscope. The pellets were polished and thermally etched prior to observation, and a

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