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Synthesis of lanthanum silicate oxyapatite materials as a solid oxide fuel cell electrolyte

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Abstract

Lanthanum silicate oxyapatites of structural formula $La_{9.33+x}(SiO_4)_6O_{2+1.5x}$ ($0 < x < 0.27$) are currently investigated for their high ionic conductivity. We have studied the synthesis of pure apatite powders, especially $La_{9.33}(SiO_4)_6O_2$ and $La_{9.56}(SiO_4)_6O_{2.34}$, by solid state reactions. We have finalized a synthesis process which limits the formation of the often encountered secondary phases La_2SiO_5 and $La_2Si_2O_7$ by using an appropriate thermal treatment of the starting mixture. Lanthanum oxyapatite powders were synthesized at a temperature much lower (1200 °C) than that used in the conventional powder solid-state synthesis routes ($T > 1600$ °C). X-ray diffraction, scanning electron microscopy and specific surface area measurements were used to analyze the structural and microstructural changes of the as prepared powders heated at different temperatures. Electrical characterization of pure sintered materials was conducted and showed that the incorporation of extra oxide ions, corresponding to the $La_{9.56}(SiO_4)_6O_{2.34}$ composition, enhanced the ionic conductivity by one order of magnitude when comparing to that of the $La_{9.33}(SiO_4)_6O_2$ sample.

Keywords: Powders-solid state reaction; Ionic conductivity; Apatite; Fuel cells $La_{9.33}(SiO_4)_6O_2$

1. Introduction

Oxide ion conductors working at moderate temperatures have a huge market potential as electrolytes for solid oxide fuel cells (SOFCs). The direct conversion of chemical to electrical energy through an electrochemical reaction is allowed by this device with excellent environmental compatibilities. However, the widely used yttria stabilized zirconia (YSZ) works as electrolyte only at high temperatures (900–1000 °C). To overcome disadvantages of these high operating temperatures, other oxide ion conductors working at intermediate temperatures (600–800 °C) are actively investigated to replace YSZ.[1] Recently, significant researches have been performed on lanthanum silicates with an apatite-type structure with composition $La_{9.33}(SiO_4)_6O_2$ which exhibits high ionic conductivity at lower temperatures ($\sigma = 7.2 \times 10^{-5}$ S cm^{-1} at 500 °C and 1.4×10^{-3} S cm^{-1} at 800 °C).[2] Electrical properties could be enhanced by the incorporation of excess La_2O_3 into this structure[3–5] in order to form hypothetical $La_{9.33+x}(SiO_4)_6O_{2+1.5x}$ ($x > 0$) compositions. It is achieved by filling interstitial sites with oxide ions located near the 2a sites (0, 0, 0.25) of the $P6_3/m$ unit cell (Fig. 1). For these compositions, either La_2SiO_5 or $La_2Si_2O_7$ are easily formed as secondary phases. Once they appear, it is very difficult to eliminate them by further firing.

Studies performed on the synthesis of apatite-type lanthanum silicates by solid state reactions have indicated that repeated long thermal treatments at high temperatures are required to prepare pure apatite-type lanthanum silicate when starting from La_2O_3 and SiO_2.[4,6–9] These high temperatures present some disadvantages such as a poor control of the morphology and particle size. To overcome these problems, other methods have been developed such as mechanochemical synthesis and sol–gel route.[2,10–12] However, the sol–gel route implies several heating steps to promote the formation of a gel and ensure the removal of all the organic components. Mechanochemical synthesis needs a long milling time (higher than 9 h) of the starting mixture.

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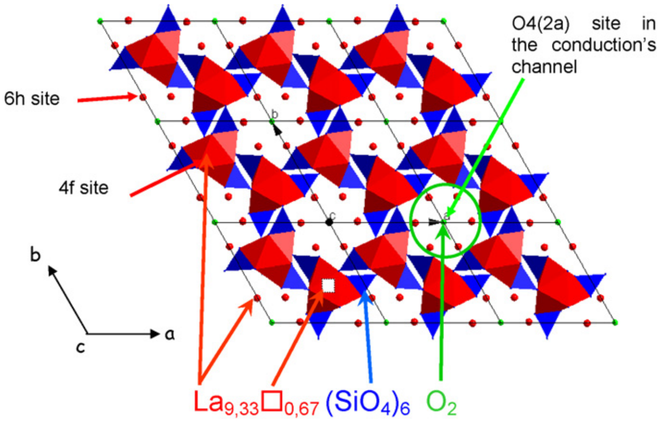

Fig. 1. *c*-Axis view of the crystal structure at room temperature of $La_{9.33}\square_{0.67}(SiO_4)_6O_2$ showing the SiO_4 groups as tetrahedra and La(4f), La(6h) and O(2a) atoms as balls.

Moreover, such processes are complex because they require a huge knowledge of all synthesis parameters otherwise they could lead to the formation of a great amount of secondary phases. In addition, these processes often produce nanocrystalline powders with a low conductivity.

In this study, we describe a new faster and lower temperature method for preparing pure apatite-type lanthanum silicate from a solid-state method. The high reactivity of the lanthanum oxide against H_2O and CO_2, transforming it into lanthanum hydroxide and carbonate, obviously influences its behaviour and the reactions with other compounds as reported by several authors.[13–22] The aging in ambient air involves a bulk hydroxylation and can also lead to a carbonation reaction. The carbonation process is suggested to occur mainly through the formation of surface carbonates or hydroxycarbonates. Additionally, when the number of carbonate groups increases, they become more and more difficult to remove with the temperature.[21] Such information must be taken into account to control the reactivity of La_2O_3 with SiO_2. The formation mechanism and the properties of the final products obtained from classical solid state reaction depend on the thermal history of the reagent powders.[15] Accordingly, we have studied the reaction of the starting mixture La_2O_3/SiO_2 (with La:Si = 9.33:6) during heating using X-ray diffraction (XRD), thermogravimetry coupled with differential thermal analysis (TG/DTA) and mass spectrometry (MS) in order to manage the formation of apatite. Especially, we propose a new method to avoid the formation of any secondary phase. Via this process, we have prepared and heated at different temperatures two compositions of apatite ($La_{9.33}(SiO_4)_6O_2$ and $La_{9.56}(SiO_4)_6O_{2.34}$). The structural and microstructural changes observed along the synthesis and sintering processes have been investigated using XRD and scanning electron microscopy (SEM). Ionic conductivity properties of the sintered materials have been measured and discussed.

2. Experimental

The apatite-type lanthanum silicates $La_{9.33+x}(SiO_4)_6O_{2+1.5x}$ ($x = 0$ and 0.23) were prepared by solid state reaction using high purity La_2O_3 (Aldrich, 99.9%) and SiO_2 (Prolabo, 99%) powders. La_2O_3 was previously dried at 800 °C for 30 min in order to eliminate lanthanum hydroxide and/or oxycarbonates and to determine the appropriate amount of this reagent. Oxides were first attrition milled for 3 h in ethanol at 450 rpm using a Union Process 01-Lab Attritor. Then, the ethanol was evaporated under vacuum at 45 °C. Different temperatures of calcination in the range 1200–1500 °C with a 4 h annealing time at each temperature, were tested in order to obtain these stoichiometric reactions:

$$(9.33/2)La_2O_3 + 6SiO_2 \rightarrow La_{9.33}(SiO_4)_6O_2 \qquad (1)$$

$$(9.56/2)La_2O_3 + 6SiO_2 \rightarrow La_{9.56}(SiO_4)_6O_{2.34} \qquad (2)$$

The calcined powders were uniaxially pressed (100 MPa) into pellets and then sintered in air at 1600 °C for 1 h resulting in disks with a diameter of ~10 mm and a thickness of ~2 mm. The densification of sintered materials was determined by geometrical measurements.

To investigate the La_2O_3/SiO_2 system, differential thermal analysis and thermogravimetry (DTA/TG) of the starting mixtures (with La:Si = 9.33:6) were performed using a TA Instruments SDT 2960 under helium atmosphere. The analysis of evolved gases was followed using a quadruple mass spectrometer (MS) (Pfeiffer vacuum thermostar) coupled together with the previous apparatus. The output of the mass spectrometer showed a plot of the relative intensity of a mass-to-charge ratio (noted *m*/*e* and corresponding to the molecular weight) versus the temperature.

Powders or pellets XRD patterns were recorded with a Siemens D5000 diffractometer (θ–2θ mode, Cu Kα radiation) in the 2θ range 20–60° (step size: 0.04°; time range: 45 min). The crystalline phases were identified using the International Centre for Diffraction Data (ICDD) Powder Diffraction Files (PDF).

The specific surface area of powders heated at different temperatures was measured using the Brunauer, Emmet and Teller (BET) method (eight points, N_2 gas analyzer Micromeritics ASAP 2010), after degassing under vacuum at 200 °C.

Microstructural investigations were made using SEM (Hitachi S2500). The surface of samples sintered at 1600 °C was prepared before observation by polishing with a SiC paper. Then, the microstructures were revealed by a thermal etching at 1550 °C for 30 min.

Ionic conductivity properties were measured by the complex impedance method using a Solartron 1260 Impedance/Gain Phase Analyzer. Measurements were made after coating opposite sides of sintered pellets with colloidal silver lac. The samples were characterized in the 250–600 °C temperature range, using frequencies from 1 Hz to 5 MHz.

3. Results and discussion

3.1. Thermal behaviour of La_2O_3/SiO_2 mixture

The mixture containing La_2O_3 (previously dried at 800 °C for 30 min) and SiO_2 (with La:Si = 9.33:6, Eq. (1)) was milled by attrition for 3 h in ethanol. In spite of such a care, La_2O_3