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Influence of the microstructure on the bulk and grain boundary conductivity in apatite-type electrolytes

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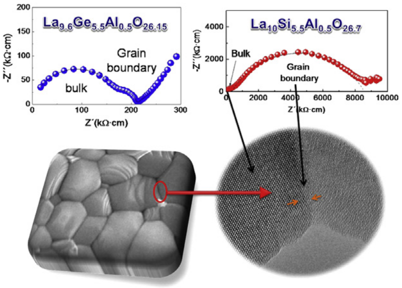
HIGHLIGHTS

- The bulk conductivity of silicate apatites depends on both porosity and sintering temperature.
- The bulk conductivity of silicates is more affected by the porosity than the grain boundary one.
- The conductivity of gemanate apatites is little affected by the ceramic microstructure.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicate and germanate apatites have attracted great interest because of their high ionic conductivity for fuel cells and other electrochemical applications. The values of conductivity of these materials are comparable or even higher than those of $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ), but vary depending on the synthetic method used and the level of densification. In order to evaluate the influence of the microstructure on the transport properties of apatite-type electrolytes, $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ (LSA) and $La_{9.6}Ge_{5.5}Al_{0.5}O_{26.15}$ (LGA) ceramics with different porosity and average grain size were prepared by varying the sintering temperature and time. Impedance spectroscopy was used to study separately both the bulk and grain boundary contributions from the overall conductivity. The bulk and grain boundary conductivities of silicates resulted highly dependent on both the porosity and the sintering temperature, on the contrary, the conductivity in germanates is barely affected by the microstructure.

1. Introduction

Ionic conductors based on silicates and germanates with apatite type structure are alternative electrolytes to the conventional yttria-stabilized zirconia to operate in Solid Oxide Fuel Cells (SOFCs) in the intermediate temperature range (600–800 °C) [1–4]. The oxide ion conductivity in these materials occurs mainly via oxygen interstitials with preferential *c*-axis conduction in comparison to

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oxygen vacancy migration in fluorite and perovskite-based electrolytes [5–13].

The conductivity of several Ge-based apatites has been reported to be higher compared to the analogous silicates [14–20]. Nevertheless, silicates have been studied more extensively due to several problems related to the high cost of germanium and volatilization losses at high sintering temperatures [21]. One of the major limitations for practical application of apatite silicates lies on the difficulty in preparing dense ceramics. For instance, the archetype compound $La_{9.33}(SiO_4)_6O_2$ synthesized by conventional solid-state reaction requires sintering temperatures of 1600–1700 °C. In order to overcome this drawback, alternative sintering processes have been proposed such as hot-pressing technique and spark-plasma [22–25]. Another approach is to use precursor routes, e.g. reactive sintering, sol–gel, freeze–drying, etc., however, the sintering temperature necessary to obtain dense ceramics is still high ~1500–1600 °C [26–40].

It is well-known that the conductivity of apatite silicates is highly dependent on the synthesis method and porosity as occurs in other solid electrolytes, e.g. $BaZrO_3$, but these effects appear somewhat mitigated in the analogous germanates [18]. Focussing on the simplest oxy-apatite stoichiometry, $La_{9.33}(SiO_4)_6O_2$, the reported conductivities for dense ceramics (>90% of relative density) vary in a broad range from 3.2×10^{-5} to 7.3×10^{-3} S cm^{-1} at 700 °C, depending on the synthesis method, temperature and the resulting densification and grain size [28–30].

The influence of the porosity on the electrical properties of $La_{9.33}(SiO_4)_6O_2$ has been investigated by Panteix et al. and surprisingly the grain interior resistance was more affected by the porosity than that of the grain boundary [24]. Dense samples with the same composition were prepared by Porras-Vázquez et al. using different methods (conventional, spark-plasma and reactive sintering) and the conductivity resulted to be seriously dependent on the synthesis route used [41].

Due to the difficulty to obtain dense apatites, a detailed study of the effects produced by both the porosity and grain size on the grain interior and grain boundary contributions to the conductivity of these materials has not yet been fully studied and understood. This requires samples prepared via the same synthetic method with different degree of porosity and grain size. Therefore, the aim of this work is to prepare lanthanum germanate and silicate apatites with controlled porosity and grain size by varying both the temperature and sintering time to obtain new insights of the role of the microstructure on the grain interior and grain boundary contributions of the conductivity. Small amounts of transition metals (e.g. Co, Cu, Al and Zn) were also used as sintering aids to improve the densification at lower temperature.

The compositions $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ (LSA) and $La_{9.6}Ge_{5.5}Al_{0.5}O_{26.15}$ (LGA) were chosen for this study because they exhibit high ionic conductivity without any phase transition in the whole temperature range studied (150–800 °C) [18,42–44].

2. Experimental

2.1. Synthesis

Polycrystalline powders of $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ (LSA) and $La_{9.6}Ge_{5.5}Al_{0.5}O_{26.15}$ (LGA) electrolytes were synthesized by a freeze–drying precursor method of stoichiometric cation solutions with ethylenediaminetetraacetic acid (EDTA) as complexing agent. Starting materials used as reagents were as follows: La_2O_3 (99.99%), SiO_2 (99.99%), amorphous GeO_2 (99.99%), $Al(NO_3)_3 \cdot 9H_2O$ (>99%) and EDTA (99.5%), supplied from Sigma–Aldrich. Lanthanum oxide was precalcined at 1000 °C for 2 h to achieve dehydration and decarbonation. Aluminium nitrate and germanium oxide, which are hygroscopic, were previously studied by thermogravimetric analysis to determine the correct cation composition of these reagents.

The cation solutions were obtained through different procedures as a function of the tetravalent cation:

i) A precursor of $La_{10}Si_{5.5}Al_{0.5}O_{26.75}$ (LSA) was firstly prepared by reaction sintering. Reagents were mixed for 1 h in a Fritsch ball mill (model Pulverisette 7) at 100 rpm with ethanol. The powders were dried at 60 °C, pelletized and then heated at 1300 °C for 5 h at a heating/cooling rate of 5 °C min^{-1}. Under these conditions, only partial reaction of the starting materials occurs. The pellet was ground in an agate mortar and dissolved in diluted nitric acid using a hot-plate with continuous stirring. The mixture of reactants was firstly heated because silica is not soluble in nitric acid, whereas the intermediate compounds formed at high temperature are soluble in acid. After that, an aqueous stoichiometric cation solution was obtained adding EDTA in a ligand:metal molar ratio of 1:1. The solution pH was adjusted to 7 by adding ammonia. The volume and cation concentration of the resulting solution were about 200 ml and 0.12 M of La^{3+} respectively. This solution was dropped and frozen in liquid nitrogen and the resulting ice crystals were dehydrated by vacuum sublimation in a freeze–dryer for 2 days. The amorphous precursor powders were immediately calcined at 300 °C to prevent rehydration and to produce the combustion of the organic material. A second thermal treatment at 1100 °C was necessary in order to remove the residual organic species and to achieve crystallization of the compounds.
ii) Precursor powders of $La_{9.6}Ge_{5.5}Al_{0.5}O_{26.15}$ (LGA) were prepared by dissolving the amorphous GeO_2 and $Al(NO_3)_3 \cdot 9H_2O$ in distilled water, whereas La_2O_3 was dissolved in diluted nitric acid. These solutions were mixed in stoichiometric amounts and EDTA was added in a 1.5:1 ligand:metal molar ratio. The dried precursor was obtained by freeze–drying as described previously. Further experimental details on the synthesis can be found elsewhere [45,46].

2.2. Powder diffraction

X-ray powder diffraction (XRD) patterns were collected with a X'Pert MDP PRO diffractometer (PANalytical) equipped with a Ge(111) primary monochromator and the X'Celerator detector, using CuKα_1 radiation ($\lambda = 1.54059$ Å). The overall measurement time was approximately 4 h per pattern to have good statistics over the 10–100° (2θ) angular range, with 0.0167° step size. Rietveld refinements of the XRD patterns were performed using FULLPROF software [47]. The fits were performed using a pseudo-Voigt peak-shape function. In the final cycles, the usual profile parameters (scale factors, background coefficients, zero-points, half-width, pseudo-Voigt and asymmetry parameters for the peak-shape) were refined. The occupation numbers and isotropic temperature factors were refined separately due to their strong correlation.

2.3. Densification and microstructural characterization

Ceramic with different relative density and grain size were obtained by adjusting the sintering temperature and time. For this purpose, the polycrystalline powders of LGA and LSA calcined at 800 and 1100 °C respectively were uniaxially pressed at 125 MPa into disks of 10 mm of diameter and 1.5 mm of thickness and then sintered in the temperature range of 1400–1600 °C for LSA samples and 1000–1200 °C for LGA samples for times between 15 min and 5 h.