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Journal of the European Ceramic Society 33 (2013) 2251–2258

www.elsevier.com/locate/jeurceramsoc

On the influence of silica type on the structural integrity of dense $La_{9.33}Si_2Ge_4O_{26}$ electrolytes for SOFCs

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Available online 5 February 2013

Abstract

Apatite-type rare earth based oxides, such as R-doped lanthanum oxides of general formula $La_{9.33}(RO_4)_6O_2$ with R = Ge, Si, exhibit high ionic conductivity and low activation energy at moderate temperatures, when compared to the yttria-stabilized zirconia electrolyte making them potential materials to be used in the range 500–700 °C, for intermediate temperature solid oxide fuel cells (IT-SOFCs). In this study, dense oxyapatite-based $La_{9.33}Si_2Ge_4O_{26}$ electrolytes have been successfully prepared either by electrical sintering at 1400 °C or microwave hybrid sintering at 1350 °C for 1 h from La_2O_3, SiO_2 and GeO_2 powders dry milled at 350 rpm for 15 h in a planetary ball mill. The densification behaviour of the apatite-type phase synthesized by mechanical alloying was found to be dependent on the grade of SiO_2 used: either pre-milled quartz powder or amorphous nanosized fumed silica. The influence of the silica type on the $La_{9.33}Si_2Ge_4O_{26}$ integrity was assessed by dynamic Young's modulus, microhardness and indentation fracture toughness measurements. A good correlation between the degree of densification (as observed by SEM/EDS) and the resulting mechanical properties could be established. Pre-milling of quartz powder has favoured higher densification rates to be attained suggesting that both Fe content, resulting from the dry milling (as determined by PIXE analyses) and crystallinity of SiO_2 do promote densification of these electrolytes thereby improving their structural integrity.

Keywords: Oxyapatite; Electrolyte; IT-SOFC; Mechanical properties; Microwave sintering

1. Introduction

Among the several types of fuel cells – devices that convert a chemical fuel directly to electricity – solid oxide fuel cells (SOFCs) are considered the most promising ones due to their high conversion efficiency, fuel flexibility and environmental compatibility.[1] However, SOFCs must be economically competitive to be commercially viable. Cost reduction requires drastic decrease of the operating temperature, typically within the range 800–1000 °C, which, in turn, is determined by the ionic conductivity of the electrolyte. Low cost materials with acceptable ionic conductivity at intermediate temperatures capable of replacing standard electrolytes such as yttria stabilized zirconia (YSZ) without loss of cell performance are needed. Apatite-type oxide phases including R-doped lanthanum oxides of general formula $La_{9.33}(RO_4)_6O_2$ with R = Ge, Si, are being regarded as candidate materials for electrolyte in SOFCs due to their high ionic conductivity between 600 and 800 °C.[2–4]

Besides high conductivity, the electrolyte must also be pore-free and have good mechanical properties at the operating temperature.[1] In a recent study, mechanical properties of dense apatite $La_{9.33}Si_2Ge_4O_{26}$ fabricated from nanopowders synthesized by mechanical alloying (MA) followed by conventional sintering at 1300–1400 °C were evaluated.[5] In the present work, the mechanical properties were determined on MA nanopowders of the same composition, densified by microwave (MW) hybrid sintering at 1350 °C. Microwave heating effect was discovered in 1946 and has been applied in a wide range of fields. Among the various applications are high temperature materials processing (>500 °C), namely sintering of metal/ceramics, solid state reactions and solid state phase transition.[6] Unlike in conventional methods where heat is transferred by the mechanisms of conduction, radiation and convection, in MW heating, three different heating features are known, specifically the internal heating, the rapid heating and the selective heating. These features allow widening of the range of industrial applications of MW heating. Likewise, the so-called "non-thermal effect"

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0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.12.024