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Powder synthesis, processing and characterization of lanthanum silicates for SOFC application

E. Jothinathan, K. Vanmeensel, J. Vleugels*, O. Van der Biest

Department of Metallurgy and Materials Engineering, Kasteelpark Arenberg 44, B-3001 Heverlee, Leuven, Belgium

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ABSTRACT

Recent studies have shown that rare earth silicates exhibit higher oxygen conductivity at lower temperatures (500–800 °C) compared to traditional yttria-stabilized cubic zirconia. Among the rare earth silicates, doped lanthanum silicates are known to exhibit higher ionic conductivity. The difficulty in sinterability of these powders combined with the fact that the electrolyte material should be sintered onto a porous anode material in a single sintering step to produce SOFC half cells requires very fine starting powders with high sinterability at lower temperatures (1000–1200 °C). In this paper, we report on the synthesis of lanthanum silicates doped with aluminium or iron using the sol–gel process. Using this fairly simple and quick process, nanometer sized powders with an average grain size below 100 nm have been synthesised, while the intrinsic nanostructure could be maintained in the fully densified electrolyte material after pulsed electric current sintering (PECS) at 1100–1200 °C.

1. Introduction

Apatite type rare earth silicates/germanates have been reported to have high oxygen ion conductivity in the 800–1000 °C range, which makes them a promising electrolyte material for intermediate temperature solid oxide fuel cells (SOFC) [1–3]. The general formula is given by $M_{10}(XO_4)_6O_{2\pm y}$, where M is a metal such as a rare-earth or an alkaline-earth metal, and X is a p-block element such as P, Si, or Ge. The crystal structure comprises isolated XO_4 tetrahedra arranged so as to form two distinct channels parallel to the *c*-axis. The smaller of these channels are occupied by M cations, while the larger channel contains oxide ions [1].

The apatite structure in general is flexible to a wide variety of substitution particularly on the rare-earth element sites, and the conductivity is very sensitive to the doping regime and cation/anion non-stoichiometry. Widely reported is the powder processing and sintering of undoped lanthanum silicate $La_{9.33}Si_6O_{26}$ [4–7]. Abram et al. [8] and Takeda et al. [9] reported that aluminium doping on the Si site increases the conductivity of the material in comparison to undoped lanthanum silicates. The introduction of aluminium, though beneficial to the conductivity, decreases the sinterability of the powder. Similarly, doping with iron increases the conductivity with increasing oxygen content and lowers the densification temperature [10]. Solid-state synthesis of the powder leads to powders of large particle size and with modest sinterability. Low temperature chemical routes like sol–gel are known to allow production of nanometer size powders [4], which increases the sinterability of the powders. In this paper we report on the synthesis and sintering studies of aluminium or iron-doped lanthanum silicates prepared by the sol–gel technique.

2. Experimental procedure

2.1. Powder preparation

Powders with $La_{9.83}Al_{1.5}Si_{4.5}O_{26}$ (LASO) and $La_{9.83}Fe_{1.5}Si_{4.5}O_{26}$ (LFSO) composition were prepared using the sol–gel route. The method involves mixing of stoichiometric ratios of the corresponding metal nitrates and tetraethylorthosilane (TEOS). The mixture is stirred until the nitrate salts together with the TEOS forms a clear solution. The temperature of the solution is subsequently raised to 50 °C and citric acid and ethylene glycol are added as polymerising agents to the solution. The mixture is kept under constant magnetic stirring for 60 min while the temperature is maintained at 50 °C. After 60 min, mixing is stopped, the temperature is raised to 70 °C and the solution is left at this temperature until the polymerisation reaction is completed and the gel is formed. The gel is transferred to an alumina crucible and calcined at 900 °C for 8 h, resulting in phase pure crystalline powder.

2.2. Characterization

Thermo gravimetric analysis (TGA/DTA, DTA 1600, T.A. Instruments, USA) of the gel is carried out under flowing oxygen (100 ml/min) with a heating rate of 5 °C/min up to 1000 °C. The phase purity, crystallinity and crystal structure of the powders are checked using X-ray diffraction (XRD, Seifert-3003 Germany). The measurements were done using Cu-Kα radiation (40 kV to 40 mA) with a step size of 0.02° and counting time of 2 s. Microstructures and particle size of the sintered pellets and powders were examined by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands), equipped with an energy dispersive analysis system (EDS, EDAX, The

* Corresponding author. Tel.: +32 16 321244; fax: +32 16 321992.
E-mail address: jozef.vleugels@mtm.kuleuven.be (J. Vleugels).

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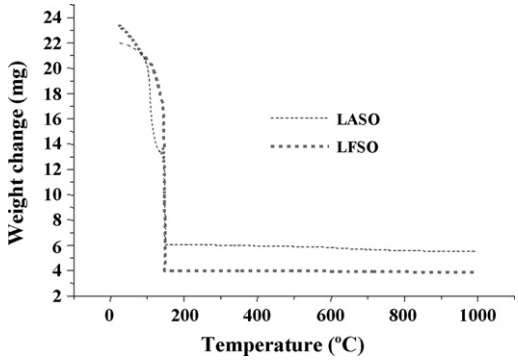

Fig. 1. TGA of LASO and LFSO gels.

Netherlands) for compositional analysis. Particle size measurements were done by means of laser diffraction (Mastersizer Microplus, Malvern, Germany) and dilatometry studies (Netzsch 404, Germany) were performed on powder pellets to find the appropriate sintering temperature. Powders are pressed to form pellets of dimension 15 mm × 10 mm by uniaxial and cold isostatical pressing (CIP) at 300 MPa. The tests are carried out in air from room temperature up to 1600 °C with a heating rate of 3 °C/min. The densities of the samples were measured according to the Archimedes principle.

2.3. Sintering

The doped lanthanum silicates were conventionally pressureless sintered (Nabertherm, Germany) in air with heating and cooling rates of 20 °C/min and pulsed electric current sintered (PECS, HP D 25/1, FCT Systeme, Germany) in vacuum with a heating rate of 100 °C/min. Pellets for conventional sintering are prepared in the same way as for the dilatometer test. The pellets have a green density of about 43%.

3. Results and discussion

The TGA curves of the LASO and LFSO gels, shown in Fig. 1 demonstrate that the major weight loss occurs below 700 °C. The weight loss in the 800–900 °C range is 0.23% and 0.14% for the LASO and LFSO gels respectively. The weight loss in the 900–1000 °C range was 0.08% for both material grades. Since there is no significant weight loss above 900 °C, the gels were subjected to single step calcination at 900 °C.

The X-ray diffraction patterns of the calcined powders are shown in Fig. 2. The patterns perfectly match JCPDF card 49-0443, which is the standard pattern for undoped lanthanum silicate ($La_{9.33}Si_6O_{26}$), indicating that the powder does not have any undesired secondary phases. The crystallite size is 32 nm, as calculated according to the Scherrer formula [11].

The highly agglomerated calcined powders require a multidirectional mixing step with zirconia milling balls in ethanol to break up the agglomerates. SEM images of the powder after calcination and after 48 h of milling are shown in Fig. 3. EDAX compositional analysis confirmed a homogeneous composition. The average powder particle size was measured to be 0.36 μm, as shown in Fig. 4.

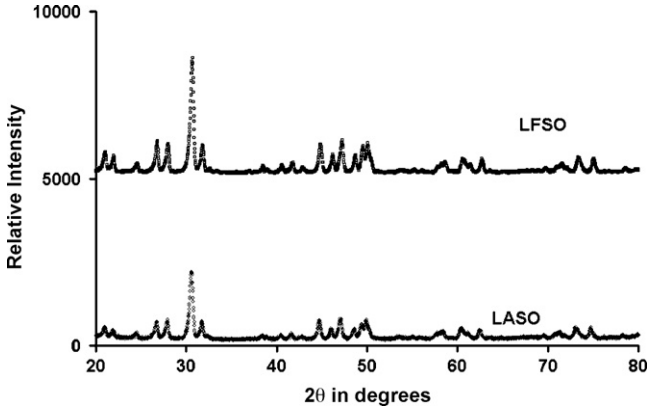

Fig. 2. XRD patterns of the powders prepared using sol–gel.

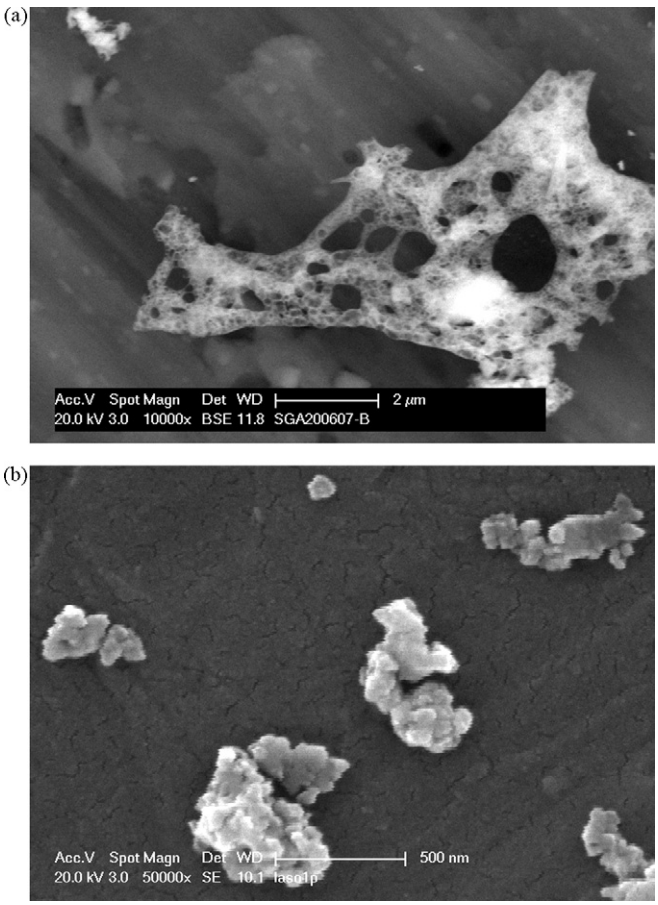

Fig. 3. SEM images of the calcined powder before (a) and after milling (b).

The dilatometer curves of the LASO and LFSO powders show an onset of densification at 1400 °C, as shown in Fig. 5. To achieve closed porosity when pressureless sintering, the sintering temperature and time required is 1550 °C for 5 h in the case of Al-doped apatites. In the case of Fe-doped apatites, the temperature required is 1500 °C for 5 h. Though there is not much difference in the slope of the dilatometer curves between the two compositions (Fig. 5), sintering is easier for the iron containing apatites. The cross-section of the sintered samples after 5 h at 1550 °C and 1500 °C is shown in Fig. 6a and b, revealing that the grain size of the LFSO is smaller than for the LASO grade. Sintering temperature and time required for powders of similar composition prepared by solid-state synthesis is 1600 °C for 10 h [10,12]. The reduction in the required sintering

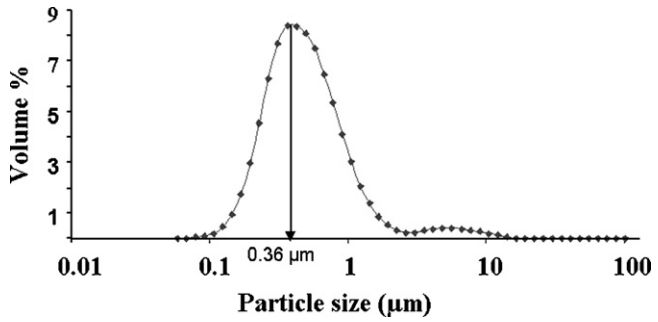

Fig. 4. Particle size distribution of the LASO powder.

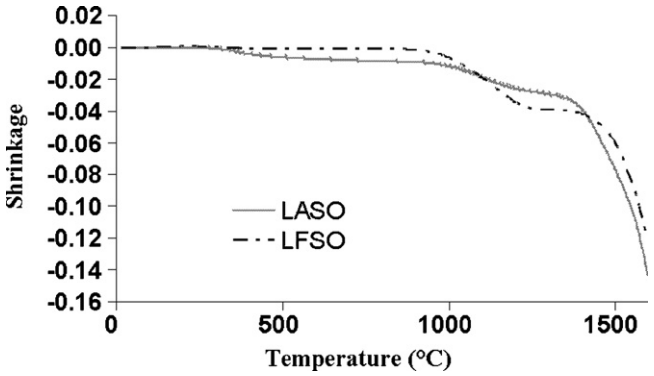

Fig. 5. Dilatometer curves for LASO and LFSO powders.

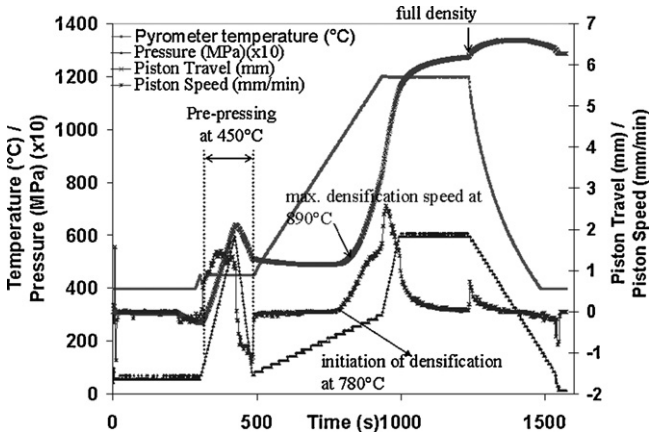

Fig. 7. Shrinkage of the LASO powder during PECS.

time is due to the nanometer size of the powders, as a result of the sol–gel processing. The operation of the fuel cell requires the electrolyte to be completely dense and the electrodes to be porous. In the case of anode supported SOFC, a thin layer of electrolyte material is processed on the anode substrate and co-sintered. The process of co-sintering the anode and electrolyte layer requires a reduction in sintering temperature down to a level at which the anode remains porous.

The conventional sintering experiments however reveal that the LASO and LFSO electrolyte powders cannot be densified to closed porosity at temperatures below 1500 °C, a temperature at which the anode material will completely densify. To overcome the low temperature densification problem, pressure assisted sintering, i.e., pulsed electric current sintering (PECS) was attempted. PECS, commonly known as spark plasma sintering (SPS) or field assisted sintering (FAST), has the potential of densifying powders with nanosized or nanostructured features while avoiding coarsening, which accompanies standard densification routes.

Chesnaud et al. [7] reported on PECS of undoped lanthanum silicate, obtaining full densification. As stated earlier, doping of the silicon site with aluminium is known to enhance the conductivity but hinders the densification of the powder. To perform PECS on the difficult to sinter aluminium containing apatites, a calculated quantity of powder is introduced into a graphite die surrounded by graphite paper. It is clear from the shrinkage data depicted in Fig. 7 that the onset of densification for the LASO powder starts at temperatures as low as 780 °C under loaded conditions and a maximum densification rate occurs at a temperature around 900 °C in contrast to conventional pressureless sintering where a temperature as high as 1400 °C is required for the onset of densification. The maximum applied temperature during PECS is 1200 °C for 5 min. SEM images of the cross-sectioned polished samples after thermal etching in air at 1350 °C for 30 min are shown in Fig. 6c and d. The PECS samples have a relative density ≥96% for both investigated compositions. The grain size of the material grades is in the 200–300 nm range.

The sintering temperature and time required to obtain closed porosity by conventional and PECS sintering is summarised in

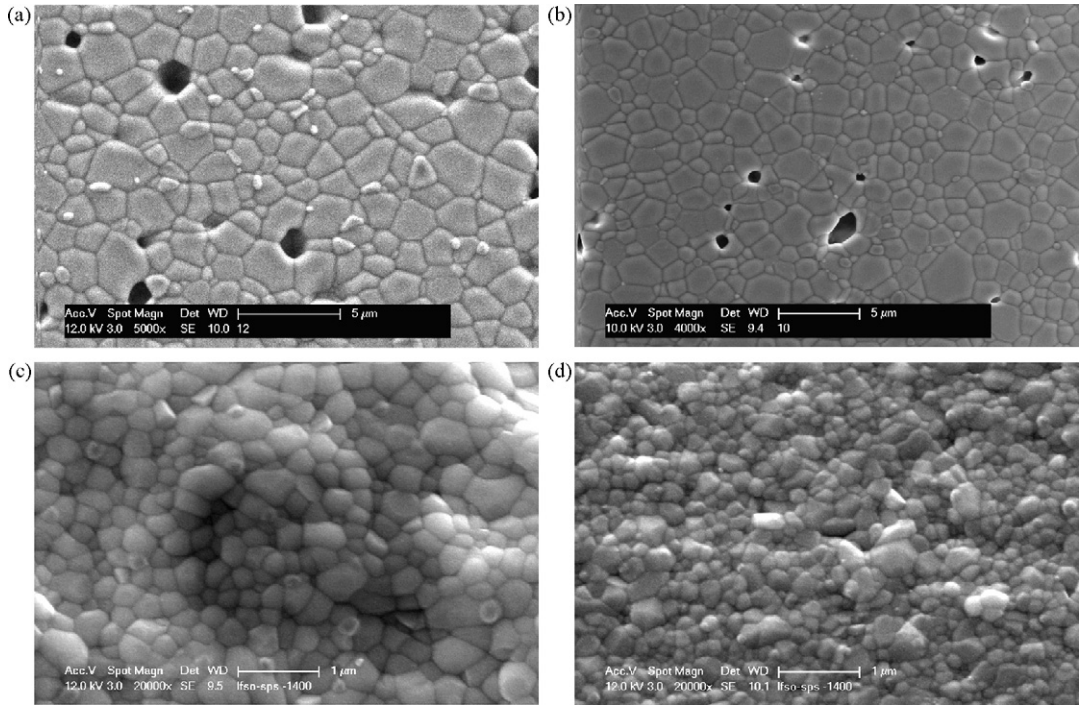

Fig. 6. Microstructure of conventionally sintered LASO (1550 °C, 5 h) (a), LFSO (1500 °C, 5 h) (b) and PECS (1200 °C, 5 min) LASO (c) and LFSO (d).

Table 1
Comparison of sintering time and temperature required to obtain closed porosity when PECS or conventional sintering.

Composition	Temperature (°C)	Sinter time (min)	Sintering technique	Density
LASO	1550	300	Conventional	>95%
LASO	1200	5	PECS	>96%
LFSO	1500	300	Conventional	>96%
LFSO	1100	5	PECS	>96%

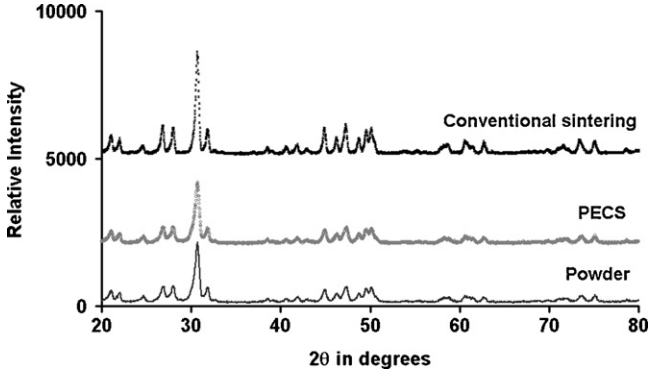

Fig. 8. XRD pattern of the LASO powder and sintered samples.

Table 1, which clearly indicates the advantage of PECS. The X-ray diffraction pattern of LASO starting powder is compared with the PECS and conventionally sintered ceramic in Fig. 8, revealing that no additional phases are formed in both the sintering techniques. Microstructures of the conventional and PECS sintered LASO are given in Fig. 6, indicating that the grain size is about 10 times larger in case of conventional sintering. The grain size plays an important role in the oxygen ion conductivity. Smaller grain sizes are quite unfavourable in conventional yttria-stabilized zirconia where oxygen ion conduction occurs by vacancy diffusion. The effect of a nanometer grain size in this new class of oxygen ion conduction, where conduction occurs through interstitial transport, remains to be investigated.

4. Conclusions

Highly crystalline and phase pure nanometer sized Al or Fe-doped lanthanum silicate electrolyte powders have been prepared by sol–gel processing. Two sintering techniques have been adopted for the sintering of these powders revealing that 5 h at 1500 °C (Fe-doped grade) or 1550 °C (Al-doped grade) are needed after conventional pressureless sintering in air is used, whereas closed porosity could already be obtained after pulsed electric current sintering (PECS) for 5 min at 1200 °C under a load of 60 MPa. It has also been demonstrated that it is possible to retain a grain size below 200 nm after PECS.

Acknowledgments

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