Synthesis by sol–gel route of oxyapatite powders for dense ceramics: Applications as electrolytes for solid oxide fuel cells

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Abstract

Solid oxide fuel cells have considerable interest in recent years, because of their high efficiency and environmentally friendly nature. Such systems required oxygen-conducting electrolytes and now the most common electrolyte is yttria stabilized zirconia (YSZ). This compound exhibits high oxide ion conductivity at elevated temperatures (850–1000 °C). However, this high working temperature causes problems in terms of materials selection and lifetime. One solution is to develop new oxide ions conductors exhibiting high oxide ion conductivity at intermediary temperatures (700–800 °C). Recent work has identified $Ln_{10-x}Si_6O_{26\pm z}$ (Ln = rare earths) as a good fast oxide ion conductor.

Undoped and doped $Ln_{10-x}B_6O_{26\pm z}$ (B = Si or Ge) oxides are currently prepared by solid-state methods. In that work, we propose a sol–gel process to synthesize powders of $La_{9.33}Si_6O_{26}$ type-silicated apatites. The main advantage is to decrease the crystallization temperature in comparison to the conventional methods, allowing the synthesis of reactive powders with nanometric particles size. These oxides are synthesized using silicon alkoxide and lanthanum nitride as precursors. In the litterature, no study refers to the synthesis of mixed oxides with silicon alcoxides. However, there are several studies on sol–gel synthesis of glasses with this precursor. In this study, several processing parameters have been investigated (the hydrolysis ratio, the concentration of metallic precursors in the sol and the role of organic compounds) in order to synthesize pure phases after the decomposition of the sols. Pure powders of $La_{9.33}Si_6O_{26}$ type-silicated apatites are obtained at 800 °C.

These powders were used to prepare ceramics. Several processing parameters as morphology of powders (agglomeration, particle sizes) and, heating profiles have been studied on the densification. Dense ceramics (90–95%) have been prepared at temperatures around 1400 °C. The used of sol–gel powders allow the decrease of the sintering temperature of about 200 °C.
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1. Introduction

The oxide ion conductor is an important functional material, which can be used as the electrolyte of solid oxide fuel cell (SOFC), oxygen sensors, and membranes. For SOFCs which are efficient and environmentally friendly systems,[1] ZrO_2 type-oxides are being widely investigated to provide good oxygen ion conductivity at high temperatures (900–1000 °C). These working temperatures mean that expensive superalloys or ceramics must be included in the fuel cell fabrication, increasing its cost substantially. These costs could be reduced if the operating temperature was lowered in the range of 600–800 °C, allowing the use of cheaper components such as stainless steel. To lower this operating temperature, either conventional electrolyte thickness (YSZ) can be drastically decreased or alternative electrolytic materials must be developed. In all cases, the major challenge is to ensure that the electrolyte remains fully dense so that the system is not short-circuited by gases going from one side of the cell to the other.

Layered lanthanide oxides with apatite-structure $[Ln_{10}(XO_4)_6O_{2\pm y}]$ (X = Si or Ge) have been selected as potential candidates to replace YSZ due to their high ionic conductivity at low temperature.[2–5] Further, depending on the nature of metal and rare earth materials, they present

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good chemical stability in reductive atmosphere. In this study, the $La_{9.33}Si_6O_{26}$ oxide has been investigated because of its high ionic conductivity at 700 °C. For example, Nakayama and Sakamoto have reported ionic conductivities for $La_{9.33}Si_6O_{26}$ as high as 0.01 $(S\,cm^{-1})$ at 700 °C.[2]

Previous studies on the synthesis of $La_{9.33}Si_6O_{26}$ oxides have shown that the sol–gel chemistry is safe, low-cost, low-temperature, versatile with few steps in the production process. After adjusting the processing parameters, $La_{9.33}Si_6O_{26}$ powders have been prepared in air at temperatures ranging from 800 °C to 1500 °C. Note that conventional ceramic route need temperatures around 1500 °C.

The aim of this paper is to synthesize dense ceramics made from sol–gel $La_{9.33}Si_6O_{26}$ powders. The originality of this work is to decrease the sintering temperature of these materials really down to 1500 °C by adjusting, in particular, agglomerates size and heating profile.

2. Experimental

Tetraethyl orthosilicate (TEOS, 98%) and lanthanum hexahydrate nitrate $La(NO_3)_3\cdot 6H_2O$ (98%) were obtained from ACROS company and used as received. $La(NO_3)_3\cdot 6H_2O$ was dissolved in a mixture of ethanol and acetic acid to give a clear transparent solution that remained unchanged upon storage, under room conditions. TEOS was added to the solution, and after stirring, the colour remains unchanged. The solution transformed into a rigid white gel after several hours at 90 °C. The flow-chart of the experimental procedure is shown in Fig. 1.

We have previously reported on the effect of the gel processing parameters such as the hydrolysis molar ratio $(r = H_2O/Si)$, the volumetric ratio of catalyst to TEOS and the silicon concentration on the purity of the oxyapatite phase.
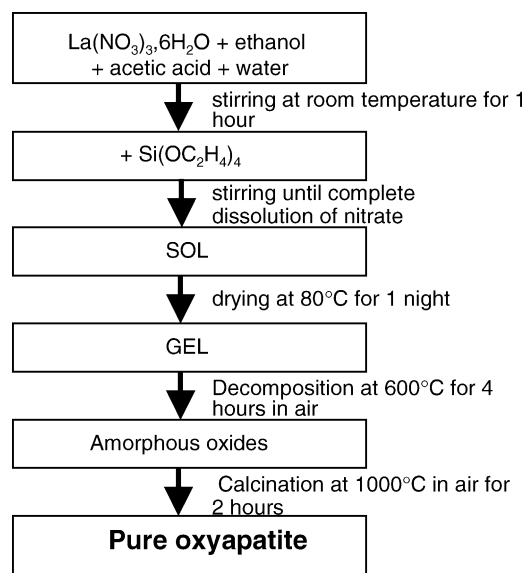
We showed that the key factor is the hydrolysis molar ratio. Pure apatite phase is obtained when the hydrolysis molar ratio is small. This phase purity is mostly correlated to the gel homogeneity.

The gels are heat-treated at 600 °C before being calcined at 1000 °C. In some experiments, some of these apatite powders were ground in water by attrition milling using YSZ balls of 2 mm diameter. Milling was carried out for 2 h, producing non-agglomerated powders.

The as-synthesized powders (with or without attrition) were then pressed into pellets (diameter, 20 mm; thickness, 2 mm; 310 MPa). For dilatometric experiments, characteristics of the pellets are: diameter, 6 mm; thickness, 2 mm; pressure, 520 MPa. Sintering behaviour of the green pellets was measured using a Netzch 402 E dilatometer. Experiments were conducted in air using an alumina sample holder with a heating rate of 1.3 °C/min. Plots corresponding to the length change versus temperature were drawn.

The green pellets were then sintered at different temperatures (1200 °C, 1400 °C, 1500 °C) with a heating rate of 50 °C/h in air. The holding time at the selected temperatures was 20 h and the cooling rate 100 °C/min. The weight changes of pellets were registered on a Precisa 205 A Balance with an accuracy of 0.1 mg and the size measurements were carried out using the Mitutoyo micrometer (accuracy: 0.001 mm).

PXRD analyses at room temperature were carried out on a Bruker D4 Endeavor diffractometer equipped with a SOL'X detector and using a Cu Kα radiation source ($K_{\alpha 1} = 1.5405$ Å and $K_{\alpha 2} = 1.5455$ Å). These experiments have been performed on each sample in order to reveal the powders crystallographic structure after heating gels at 1000 °C or 1500 °C in air. The Rietveld method and FullProf program were used for crystal structure refinement. This allows the determination of lattice parameters ($a = 9.726(3)$ Å and $c = 7.184(5)$ Å) and crystallite sizes. From these data, the theoretical volumic mass of $La_{9.33}Si_6O_{26}$ was determined (5.3066 $g\,cm^{-3}$).

Morphology of both powders and ceramics resulting from various sintering and processing conditions was studied by scanning electron microscopy (JEOL JSM 6400) and scanning electron microscopy coupled with a field emission gun SEM-FEG (JEOL JSM 6700F).

3. Results and discussion

At first, we have synthesized ceramics with powders without pre-treatment. Linear shrinkage and differential linear shrinkage curves, during dilatometry experiments on pellets, are shown in Fig. 2. The onset of densification was above 1000 °C and two sintering steps can be observed at 1200 °C and 1400 °C. Each minimum in the differential shrinkage curve corresponds to the elimination of pores with different sizes, following the particles rearrangement: the smaller pores at the lower temperature (1200 °C) and the larger ones at higher temperature (1400 °C). These pores are related to the presence of agglomerates in the compact. In particular,
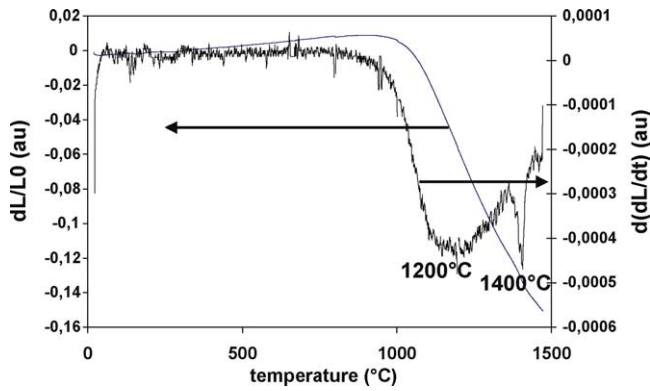

Fig. 1. Flow-chart of preparation of for $La_{9.33}Si_6O_{26}$ powders.

Fig. 2. $\Delta L/L_0$ and differential curves as a function of the heating temperature.
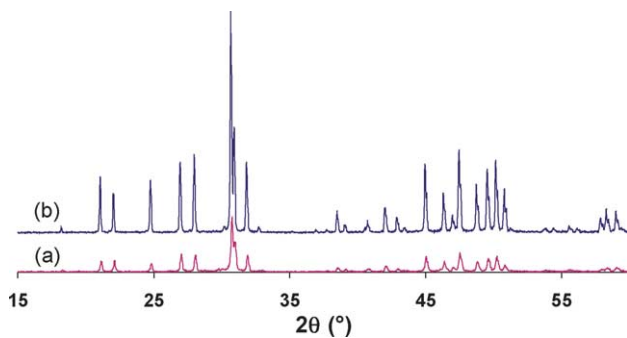

Fig. 3. X-ray diffraction pattern (Cu Kα) of La$_{9.33}$Si$_6$O$_{26}$ oxides powders heat-treated at 1000 °C (a) and ceramics heat-treated at 1500 °C (b).

the lower temperature peak corresponds to the elimination of the intra-agglomerate pores while the higher temperature peak is attributed to the inter-agglomerate pores removal.

By X-ray diffraction studies (Fig. 3), it can be seen that no impurity was observed. The apatite-structure is kept even after heat-treatment at 1500 °C in air for 20 h.

Variation of the relative densities as a function of the sintering temperature is reported in Table 1 for pellets made of sol–gel powders heat-treated at 1000 °C. The sintering temperature of 1200 °C is not sufficient to obtain good values of density. The resultant densification is poor (72%) even after a heat-treatment at 1500 °C and complete densification (95%) is not reached. This behaviour can be explained by the presence of agglomerates in the powder. Indeed, a fast increase of the grain growth at high temperature appears during the inter-agglomerates pore elimination, giving rise to the stabilization of large pores.

According to Quinelatelo works,[6] complete densification in the sintered compact is achieved for high degree of green

Table 1
Variation of the relative densities as a function of the sintering temperature

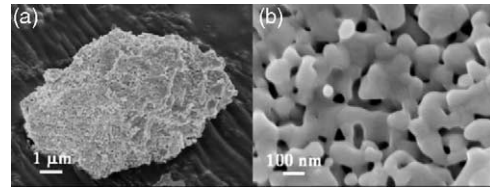| Sintering temperature (°C)	Green pellets (%)	Sintered pellets (%)
1200	50	56
1400	50	69
1500	50	72

Fig. 4. SEM-FEG feature of La$_{9.33}$Si$_6$O$_{26}$ powders calcined at 1000 °C: (a) 1 μm and (b) 100 nm.

compact homogeneity. This is mostly related to particles size and the presence of agglomerates in powders. In general, ceramics made of powders consisting of soft agglomerates achieved high densification. By the sol–gel method, it is difficult to obtain non-agglomerated powders. SEM-FEG studies confirm, for powders heat-treated at 1000 °C, the presence of agglomerates of some tens of microns (Fig. 4). Besides, it can be noticed (Fig. 4b), that, at 1000 °C, the sintering process starts: necks between grains can be observed. Thus, this result shows that the powders heat-treated at 1000 °C consist of hard agglomerates, which are not eliminated during the compaction step.[7] This explains why it is so difficult to obtain dense compacts without pre-treatment of the powders.

We have then prepared ceramics from powders with high-energy attrition millings. This technical was done to obtain soft agglomerates. SEM micrograph of La$_{9.33}$Si$_6$O$_{26}$ powder calcined at 1000 °C and then attrited for 2 h is shown on Fig. 5. It can be observed a well-dispersed powder with particles size of about 100 nm. This trend is not observed with no-attrited powders. In attrited powders, soft agglomerates are present which can be easily broken while no-attrited powders have hard agglomerates. Consequently, in ceramics made of attrited powders, the homogeneity is higher than the one obtained for ceramics with powders just heat-treated at 1000 °C.

Dilatometry curves of attrited powders pellet are shown in Fig. 6. A large peak at 1200 °C corresponds to the presence of soft agglomerates with a narrow distribution. This result is different from the one obtained for ceramics made of no-attrited powders where two steps are observed (Fig. 2).

These sintered pellets achieve relative density of 92% at 1450 °C which is higher than the one observed no-attrited powders ceramics (69%). It can be seen (Fig. 7) a micrograph of dense La$_{9.33}$Si$_6$O$_{26}$ ceramics. The grain size of dense ce-
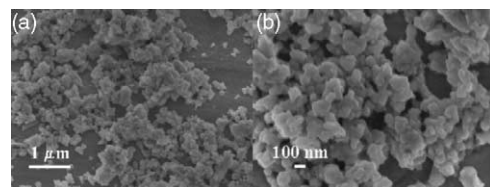

Fig. 5. SEM-FEG feature of La$_{9.33}$Si$_6$O$_{26}$ powders calcined at 1000 °C and attrition milling.
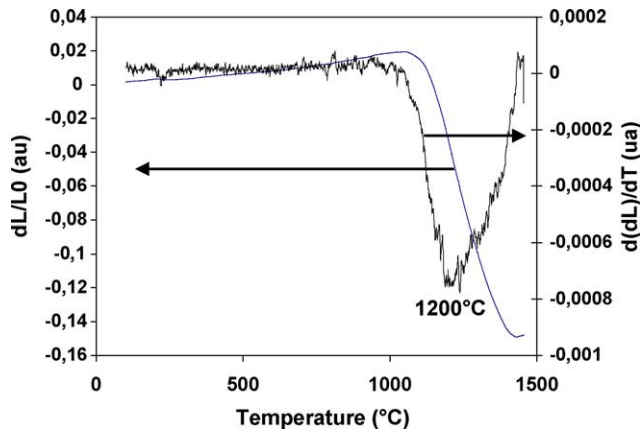
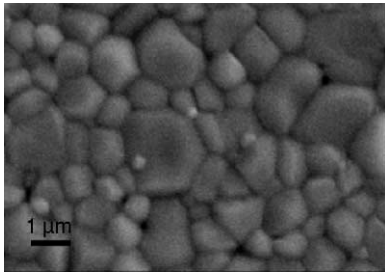Fig. 6. $\Delta L/L_0$ and differential curves as a function of the heating temperature.

Fig. 7. Scanning electron micrograph of $La_{9.33}Si_6O_{26}$ ceramics with a sintered density of 92%.

ramics lies around 0.5–3 μm, and is about 10 times more than the starting powders.

Sol–gel powders allow a decrease of 200 °C of the sintering temperature. By solid-state synthesis, this temperature is 1700 °C for density higher than 90% and, at 1500 °C, the final density is lower than 83%.[8] Till now, for oxyapatite powders synthesized by sol–gel, best densification values at 1500 °C were of 74%.[5]

4. Conclusion

Nanocrystalline powders $La_{9.33}Si_6O_{26}$ synthesized from new chemical route based on sol–gel process were used to prepare dense ceramics. The starting particles size and the sintering behaviour had a great influence on the relative density of the ceramics. It was determined, that high density (up to 90%) could be achieved after attrition milling step. The major challenge now is to verify that these ceramics remain fully dense during working cycles in order to ensure high ionic conductivity and to avoid gases mixture from one side of the cell to the other.

Acknowledgements

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