

Sol-gel Route for Synthesis of Apatite-type Lanthanum Silicate Powders

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Abstract

Oxide ion conductor is an important functional material used as the electrolyte of solid oxide fuel cell (SOFC). Zirconia types-oxides, such as yttria stabilized zirconia (YSZ), are being widely studied to give good oxygen ion conductivity. However, it works as electrolyte only at high temperatures (900-1000°C). These working temperatures mean that expensive materials must be included in the fuel cell fabrication, increasing its costs substantially. To overcome disadvantages of these high operating temperatures, other oxide conductors working at intermediate temperatures are investigated. Recent reports have indicated that rare earth based apatites are viable electrolyte materials for intermediate temperature SOFC. Lanthanide oxide with apatite-structure $[Ln_{10}(XO_4)_6O_{2\pm y}]$ (X=Si or Ge) have been chosen as potential candidates to replace YSZ due to their high ionic conductivity at low temperatures. 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 (700°C). We propose a sol-gel process to synthesize apatite-type lanthanum powders. The main advantage of this process is to decrease the crystallization temperature in comparison to the conventional methods. Tetra ethoxysilane (TEOS) and La_2O_3 were used as starting materials. The properties of the resulting apatite phases have been characterized by thermal analysis (TGA-DTA). X-ray diffraction, scanning electron microscopy and specific surface area measurements were used to analyze the structural and microstructural changes of as prepared powders. The apatite phases may be obtained at 900°C.

Introduction

For last past years, the increasing interest in development of more efficient and environmentally friendly with lowest amount pollution, to produce energy, focused on technologies as solid oxide fuel cells (SOFC). The SOFC devices allow the direct conversion of chemical to electrical energy through an electrochemical reaction. The basic components in every one SOFC unit are: a cathode, an anode and electrolyte. The anode and cathode are separated by the electrolyte which must have high oxide conductivity, low thermal expansion and good chemical compatibility with the cathode and anode materials. The commercial SOFC system use YSZ (yttria stabilized zirconia), as electrolyte [1-4]. In fact, this material has good ion conducting performances, but only at high temperatures (900-1000°C). This generates some problems, such as ageing or favored reactions at the interfaces, consequently special and expensive materials must be included in the fuel cell fabrication, increasing its costs considerably. Other electrolytes are being studied to replace YSZ such as gadolinium-doped ceria, GDC, which has higher ion conductivities at lower temperatures. Oxide ion conductors having a high ionic conductivity at relatively low temperatures have generated considerable interest for use as solid electrolytes for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Among them, the apatite-type lanthanum silicate [5,6] is characterized by a high ionic conductivity at an intermediate temperature [7]. It showed an appreciably higher conductivity than that of YSZ at relatively low temperatures below 600 °C [6,7]. Attractive characteristic of apatite-type lanthanum silicate is its unique interstitial conduction mechanism [8-10], in contrast to a vacancy mechanism, usual to the stabilized zirconia.

1. Scientific Approach

Electrolyte processing requires submicron materials with controlled morphology. From this point of view, the conventional solid state chemistry paths have a large disadvantage because of the very high synthesis temperature required, higher than 1600 °C [6,7], due to a low reactivity between lanthanum oxide and silica. La_2SiO_5 or $\text{La}_2\text{Si}_2\text{O}_7$ is easily formed as second phase. Once they formed, it is difficult to remove them by posterior firing. To overcome these problems, other methods have been developed [11,12]. Consequently developing of a new synthesis route in low temperature is the key research of the lanthanum silicate apatite. In this study we describe a new and low temperature method for preparing apatite-type lanthanum silicate from a sol-gel route. The sample composition used in this study is $\text{La}_{9.56}(\text{SiO}_4)_6$. The raw materials were lanthanum oxide tetra ethoxysilane (TEOS). TEOS in ethanol was hydrolysed with simultaneous precipitation of lanthanum hydroxide from nitric aqueous solution, using NH_4OH to a final of pH 10.5. The apatite formation from precursor was investigated by powder x-ray diffraction analyses (XRD), thermo-gravimetric differential thermal analysis (TG-DTA). It was verified from the analysis profile that apatite type lanthanum silicate was formed by heating treating at 900°C for 3h in air.

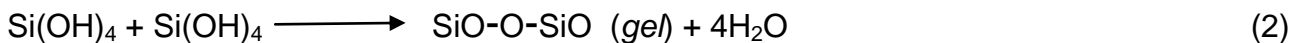
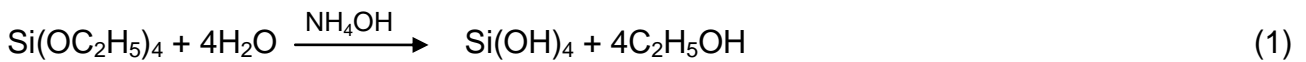
2. Experiments

Tetra ethoxysilane (TEOS, Aldrich, 98%), and lanthanum oxide La_2O_3 (99,9% Vetec), were used as received. La_2O_3 was previously calcined at 800°C until no variation of its weight. A stoichiometric mass of the calcined La_2O_3 was weighed in analytical balance (\pm

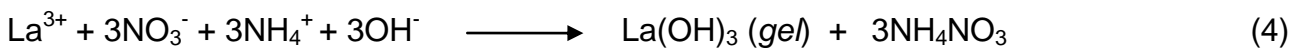
0.0001g accuracy) and dissolved in 6M HNO₃. To obtain the precursor solution of Si, a stoichiometric amount of TEOS was mixed with ethanol (PA grade). Then, the solutions of Si and La precursors were stoichiometrically mixed to achieve the final composition La_{9.56}(SiO₄)₆O₂. The resulted mixed solution was added in NH₄OH solution (25%) with vigorous and constant stirring. The amount of NH₄OH solution was previously calculated to give a final of pH 10.5. A turbid and milky sol was obtained. After total addition of the solution, the suspension mixture was kept with stirring for 5h. After that, the gel was filtered and washed with distilled water until pH of 7.0. The washed gel was dried over night at 80 and calcined to obtain apatite-type lanthanum powders, La_{9.56}(SiO₄)₆O₂. Thermal analysis of the gel was carried out on a Setaran simultaneous TG-DTA 92 instrument from room temperature to 1000^oC (5^oC.min⁻¹) under flowing air at rate 100 mL.min⁻¹. XRD analysis of the powders calcined at different temperatures were carried out on D-8 Advanced, Bruker-AXS, with CuK_α radiation in the 2θ range 20-60^o. The crystalline phases were identified from a comparison of the obtained patterns with the ICDD (international center for diffraction data) power diffraction files (PDF). The specific areas of the powders were measured by BET (Brunauer, Emmet and Teller) method on Quantachrome-Nova 1200, after degassing under vacuum at 200^oC. Microstructural investigations were made using SEM (XL 30 Philips).

3. Results

As described in the experimental section, the gel of silica is formed by hydrolysis and condensation of TEOS according to the following reactions in presence of NH₄OH as basic catalyst:



La³⁺ is precipitated with NH₄OH according to the following reaction:



The gel resulted from those above reactions ((3) and (4)) consists to the precursor of La_{9.56}(SiO₄)₆O₂. In order to determine the phase formation and transition temperatures, the precursor gel was investigated by thermal analysis as shown in Fig. 1.

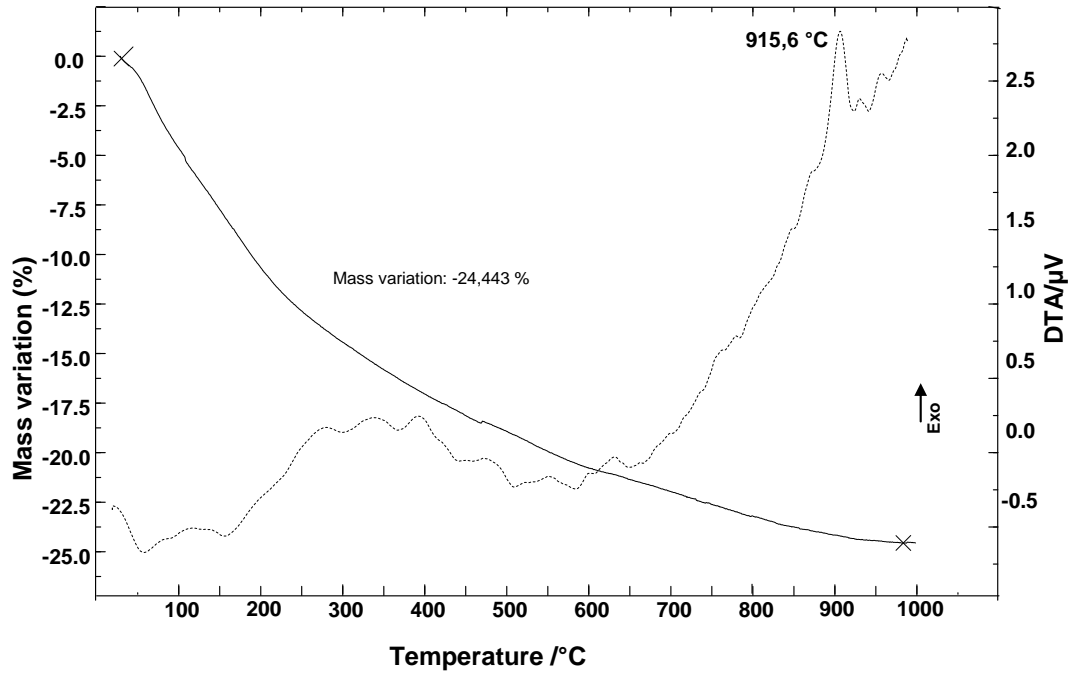


Figure 1- TGA-DTA curves of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ precursor gel.

The 24.443% mass variation observed in Fig. 1, between 25-980^oC, might be attributed to the dehydration process of the gel of silica and $\text{La}(\text{OH})_3$, and decomposition of organic residual component. According to the DTA curve, an exothermic peak is observed at 915^oC, due to the crystallization or formation of apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ phase, as confirmed by comparison of XRD patterns obtained from the gel thermal treated at 800 and 900^oC, as showed in Fig.3 and Fig. 4 respectively. From XRD diffraction pattern showed in Fig. 2, it is observed that the sample is amorphous with an indication of the formation of the apatite phase. In the XRD pattern presented in Fig. 3 it is observed that the sample is crystalline, essentially $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ apatite phase.

The result of analysis obtained by BET technique for the sample, calcined at 900^oC for 3h, presented a high specific surface area 27.3 $\text{m}^2.\text{g}^{-1}$, indicating that a powder highly reactive was achieved. This was confirmed on the SEM micrographs presented in Fig. 4, where submicron particles are observed. From Fig. 5, no appreciate changes of the particle size or the agglomerate size were verified with increasing the temperature of calcining from 800 to 900^oC.

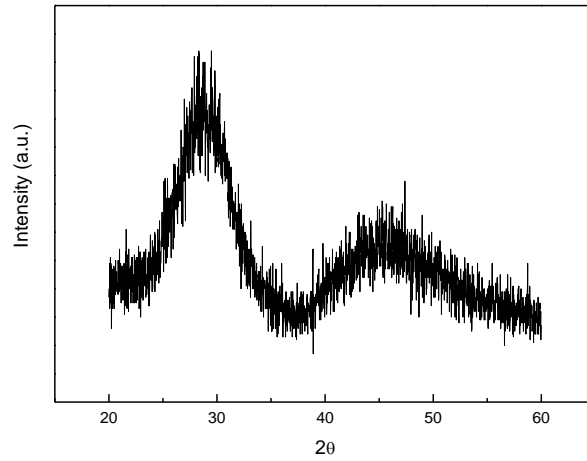


Figure 2 – XRD patterns of the precursor gel of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ after calcining at 800°C for 3h.

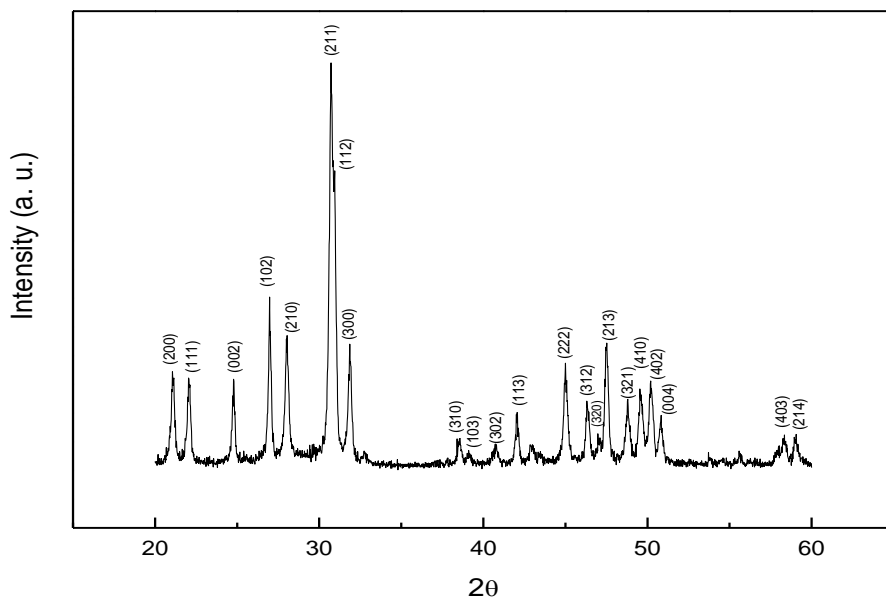


Figure 3 – XRD patterns of the precursor gel of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ after calcining at 900°C for 3h.

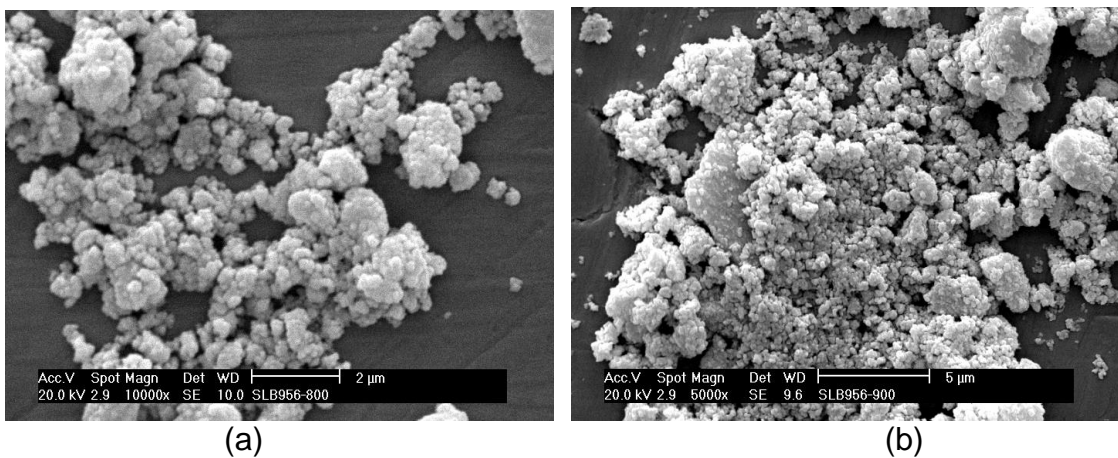


Figure 4 – SEM micrographs of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ sample calcined at 800°C (a) and 900°C (b) for 3h.

Pellet of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ was prepared from powder calcined at 800°C and then it was sintered at 1400°C for 3h. The XRD of the sintered sample is presented in Fig. 5.

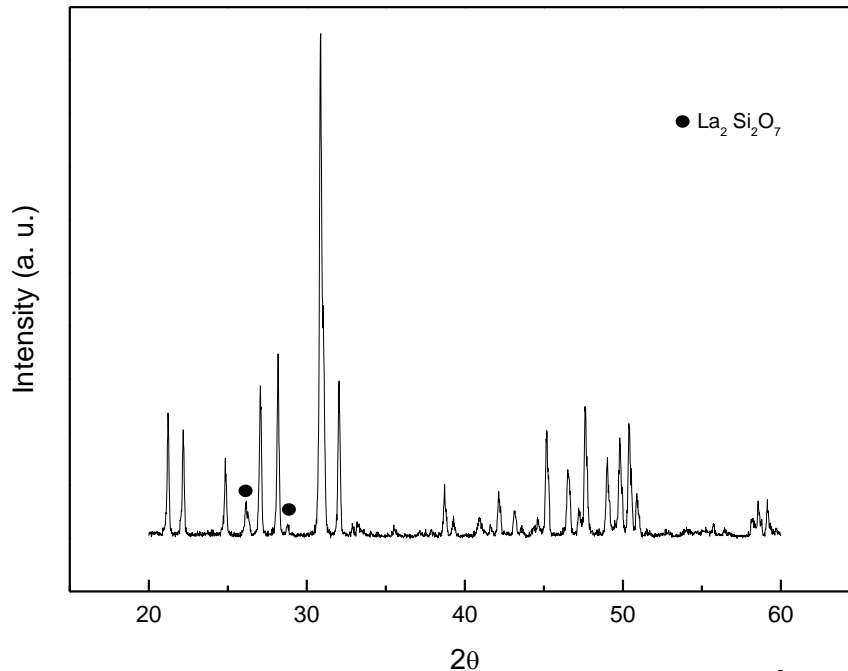
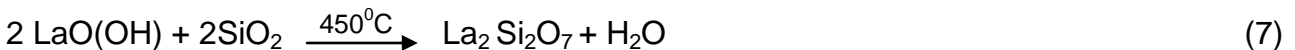


Figure 5 – XRD pattern of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ pellet after sintered at 1400°C for 3h.

By XRD patterns from Fig. 5, it can be seen that the main phase is $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ apatite phase. A secondary phase $\text{La}_2\text{Si}_2\text{O}_7$ was detected on the XRD pattern from Fig. 5. This phase was not detected on XRD pattern of calcined powder at 900°C , so it may be formed into the period after calcining and before sintering process. Some smallest amount of La_2O_3 , which was not reacted with SiO_2 , might be present in the calcined sample. The transformation of this quantity of La_2O_3 into $\text{La}(\text{OH})_3$ by H_2O vapor in the atmosphere at room temperature is inevitable:



The formation of $\text{La}_2\text{Si}_2\text{O}_7$ secondary phase may be related to the reaction between $\text{LaO}(\text{OH})$, formed during the thermal treatment of sintering process, by the dehydration (Eq. 6) of transformed lanthanum hydroxide (Eq. 5) with SiO_2 (Eq.7) (13,14,15):



Once $\text{La}_2\text{Si}_2\text{O}_7$ phase is formed it is stable up to 1750°C [16] and its elimination by high thermal treatment become visible difficult. Therefore, in order to reduce $\text{La}_2\text{Si}_2\text{O}_7$ it is essential avoid the formation of $\text{LaO}(\text{OH})$. Consequently after calcining the powder, it must be kept it in a dry atmosphere to prevent the hydration process (Eq. 5). A preheating of the furnace is recommended by a latest work (1). The formation of the $\text{La}_2\text{Si}_2\text{O}_7$ secondary phase was totally inhibited when the dry powder was kept at 130°C and placed into furnace directly at 450°C (17).

The relative density of the sintered pellet, determined by Archimedes method, was of 81%. It is a good result, considering that the ceramic was prepared from powder which was not

milled. A complete densification may be reached by high energy attrition milling to broken down the agglomerates present in the powder, after preparing the ceramic. From the obtained results, it be concluded that a new low temperature and fast sol-gel method for the preparation of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ was presented. Nanocrystalline powders $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ were synthesized. Particle size of the powder, evaluated by specific surface area ($27.3 \text{ m}^2\cdot\text{g}^{-1}$) was around 100-150 nm. The temperature of crystallization was 900°C . The sintered sample presented small amount of $\text{La}_2\text{Si}_2\text{O}_7$ secondary phase and the relative density of 81%. It is important to notice that this density was reached by ceramic prepared by sintering at 1400°C for 3h from powders without grinding. The major challenge at the moment is to investigate the means to avoid totally the formation of $\text{La}_2\text{Si}_2\text{O}_7$ secondary phase in order to obtain pure $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_2$ lanthanum silicate oxyapatite.

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