

Low Temperature Synthesis of Lanthanum Silicate Apatite Type by Modified Sol Gel Process

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Abstract. Rare earth silicate apatite type is a very important and promising material for application as an electrolyte in IT-SOFC (Intermediate Temperature Solid Oxide Fuel Cell). Lanthanum silicate apatite, $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$, exhibits high conductivity and has high efficiency, long term stability, fuel flexibility, low emissions and relatively low cost compared to yttria stabilized zirconia (YSZ), at temperatures between 600 and 800 °C. One of the problems of YSZ is its high operating temperature, which results in long starting times and problems of mechanical and chemical compatibility. The interest of investigating lanthanum silicate apatite as an electrolyte is to overcome the problems caused by high temperature operation required by YSZ electrolyte. In the present study, the sol-gel method was used to synthesize $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$. Initially, the reagents (sodium silicate and lanthanum nitrate) were mixed to obtain colloidal silica. Then, this gel containing lanthanum nitrate was thermally treated to allow the melting of lanthanum nitrate salt distributed on colloidal silica. The aim of this study was to verify if this method permits the formation of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ pure apatite phase, in order to obtain fine powders and uniform particles for further processing and obtaining a ceramic body.

Introduction

Yttria stabilized zirconia (YSZ) is the most common material used as SOFC (Solid Oxide Fuel Cell) electrolyte, because of its high oxygen ion conductivity at high temperatures in the range of 1000 °C. This high temperature requires not only expensive materials but also results in a reduction of the life time of the system due to many problems, such as thermal and chemical durability of the material, component sealing of the cell and material degradation. Extensive study is being done to develop efficient materials as electrolyte in an effort to reduce the high operating temperatures of SOFCs [1-5], in order to prolong the lifetime of the cells, reduce the cost of materials and widen the choice of materials. Rare earth apatite type has been investigated [6-8] to develop new electrolytes with high ionic conductivity at intermediate temperature. Nakayama et al. [6] reported that apatite-type structure of compositions $\text{Ln}_{10-x}\text{Si}_6\text{O}_{26+y}$ ($\text{Ln} = \text{La Sm, Nd, Dy, Gd}$, $x = 8$ to 11) materials exhibited ionic conductivity. Among these rare earth apatites, lanthanum silicate with composition of $\text{La}_{10}\text{Si}_6\text{O}_{27}$ has exhibited the highest oxygen ionic conductivity of $>10^{-3} \text{ Scm}^{-1}$ at 500 °C, which is comparably higher than that of 8 mol% yttria, doped zirconia (YSZ) electrolytes [6]. However, pure apatite-type $\text{La}_{10}\text{Si}_6\text{O}_{27}$ is difficult to obtain [9] due to the presence of secondary phases, such as $\text{La}_2\text{Si}_2\text{O}_7$, La_2SiO_5 in the binary phase diagram of $\text{La}_2\text{O}_3 - \text{SiO}_2$ system [10]. Those secondary phases decrease the ionic conductivity [11]. Both La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$ are very stable phases, difficult to remove once formed. The presence of secondary phase La_2SiO_5 during solid state reaction suggests that $\text{La}_{10}\text{Si}_6\text{O}_{27}$ is not an equilibrium phase and is not stable. On the other hand, $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ unlike $\text{La}_{10}\text{Si}_6\text{O}_{27}$ may be readily attained since it is in equilibrium with the secondary phase, La_2SiO_5 [10].

Lanthanum silicate is usually synthesized by solid state reactions by long thermal treatments at high temperatures (1500-1700 °C) [12-14]. These conditions of high temperatures and long time periods present some disadvantages such as poor control of the morphology and particle size. The

presence of the secondary phases on the final product obtained from this method [15] indicates that it may be difficult to obtain a homogeneous mixture of the oxide precursors. To overcome these problems, other methods have been developed, for example, the sol–gel route.

By the sol-gel process [16-18] apatite-type lanthanum silicate oxides are prepared at relatively lower temperatures comparing to solid state reactions. This may avoid the formation of the secondary phases due to better homogeneity of oxide precursors.

In this study a new and low temperature method for preparing apatite-type lanthanum silicate from a modified sol-gel route is described. The usual source of silica used in sol gel synthesis is TEOS (tetra ethoxysilane). In this proposed method, a sodium silicate solution was used to substitute TEOS. The use of this source of silica has not yet been reported, as to the best of our knowledge. The sample composition used in this study was $\text{La}_{9.33}(\text{SiO}_4)_6$. The raw materials were lanthanum oxide and sodium silicate solution. Sodium silicate was added to La_2O_3 dissolved in a high acidic HNO_3 solution. The resulting mixed solution was left overnight at room temperature to form gel silica. The precursor powder of $\text{La}_{9.33}(\text{SiO}_4)_6$ was obtained by thermal treatment of the gel at 900 °C for 1h followed by washing, and filtration to remove Na ions. A second calcining step at 900 °C for 4h was performed and resulting powder was compacted and sintered at 1200 and 1300 °C to obtain the ceramic body. Crystalline single phase of apatite type $\text{La}_{9.33}(\text{SiO}_4)_6$ was achieved.

Experiments

A stoichiometric mass of the calcined La_2O_3 was weighed and dissolved in 6M HNO_3 . To obtain the precursor solution of Si, a stoichiometric amount of sodium silicate was dissolved in water. The solutions of Si and La precursors were stoichiometrically mixed to achieve the final composition $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The resulting clear mixed solution was left overnight at room temperature to form gel silica by acid catalyzed hydrolysis and condensation reactions. The resulting gel was then dried on a hot plate at temperatures between 150-200 °C to obtain a white powder. This powder was then submitted to pre-calcination at 900 °C for 1h. The white powder was washed with distilled water, filtered up to 7.0 pH and dried over night at 80 °C. Afterward it was calcined at 900 °C for 4h to obtain the precursor powder of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$, that was uniaxially compacted into a pellet and sintered at 1200 and 1300 °C to obtain the ceramic body. The crystalline phases were identified from a comparison of the obtained patterns with the JCPDS (Joint Committee on Powder Diffraction Standards) files. The specific area of the powder was measured by the BET (Brunauer, Emmet and Teller) method, after degassing under a vacuum at 200 °C. The as-synthesized powders without attrition were pressed into pellets and sintered at 1200 °C and 1300 °C for 8 and 4h respectively. The microstructure of synthesized powders and ceramics were performed by the SEM. Archimedes method has been used to evaluate the apparent density of the sintered ceramic.

Results and Discussion

SEM micrographs of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ powder after calcining at 900 °C for 4h is presented in Fig. 1. In this image, dispersed fine particles ($< 3\mu\text{m}$) and the presence of hard like agglomerates of some tens of microns can be observed. Perhaps, at temperatures of 900 °C used to thermally treat the powder, the sintering process may be started and therefore promote the development of those agglomerates.

The specific surface area measured by BET method for the precursor powder $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ after calcining at 900 °C for 4h was $2.2 \text{ m}^2 \cdot \text{g}^{-1}$. This low value of specific surface area, might justify the observation above, i. e., the beginning of the sintering process.

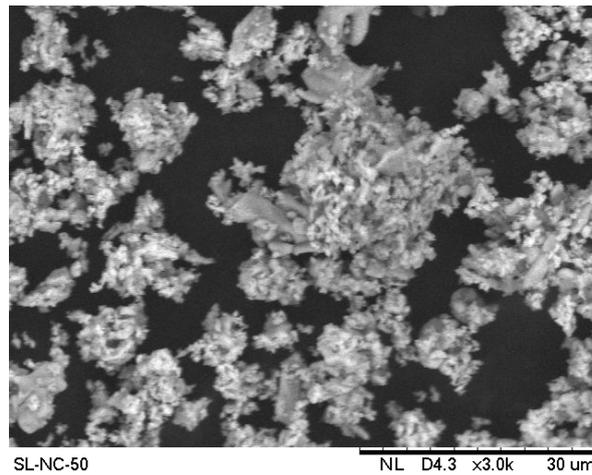


Figure 1- SEM micrographs of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ powder after calcining at 900°C for 4h.

XRD patterns of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ precursor powder calcined at 900°C for 4h and ceramic sintered at 1300°C for 4h are shown in Fig. 2.

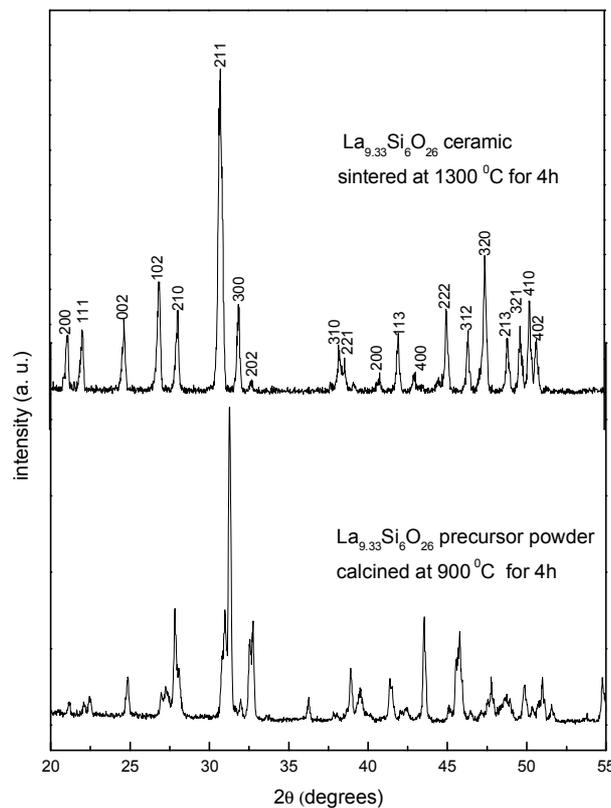


Figure 2- XRD patterns of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ precursor powder calcined at 900°C for 4h and of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ ceramic sintered at 1300°C for 4h.

By comparison of those XRD patterns with the that of the apatite lanthanum silicate JCPDS 49-0443, it can be noticed that the apatite phase is not present in the $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ XRD precursor powder. XRD of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ ceramic, sintered at 1300°C for 4h, has the same pure apatite structure characteristic peaks (JCPDS 49-0443), and no significant impure peaks are present. The XRD patterns of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ ceramic sintered at 1200°C for 8h showed the same pure apatite structure as the patterns of the sample sintered at 1300°C .

SEM micrographs of the ceramic sintered at 1200 °C for 8h (Fig. 3a) and of the that sintered at 1300 °C for 4h (Fig. 3b) from precursor powder of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ calcined at 900 °C for 4h are shown in Fig. 3.

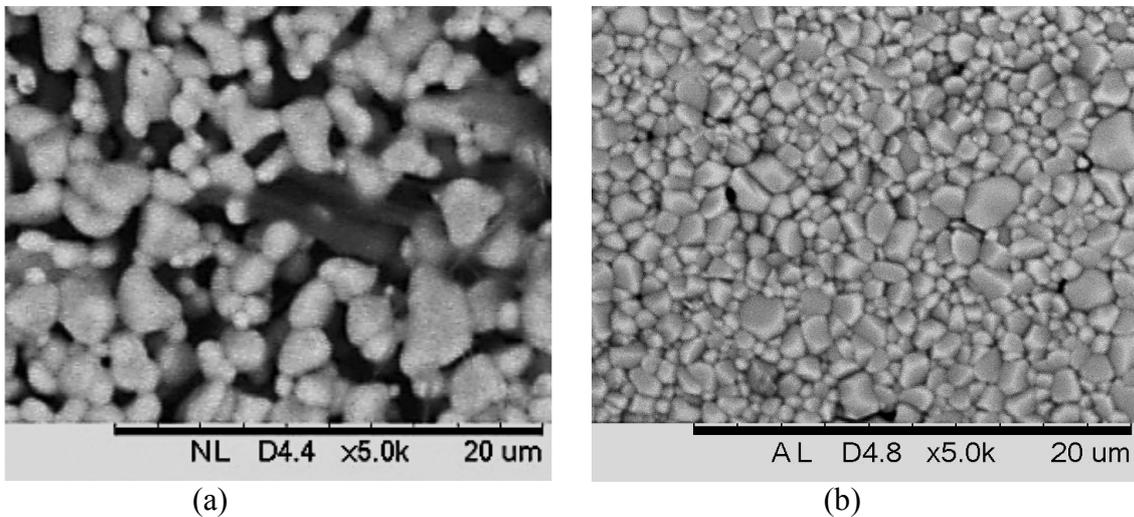


Figure 3- SEM micrographs of the ceramic sintered at 1200 °C for 8h (a) and of the ceramic sintered at 1300 °C for 4h (b) from precursor powder of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ calcined at 900 °C for 4h.

The SEM micrograph of the ceramic sintered at 1200 °C, Fig. 3 (a), clearly shows a porous microstructure, while in the image of the ceramic sintered at 1300 °C, Fig.3 (b), highly dense grains with well-defined boundaries are present and the porosity is negligible. Apparently, the grain size of sintered ceramic at 1200 °C is greater (in average $> 2 \mu\text{m}$), than that of the ceramic sintered at 1300 °C, that is in average $< 2 \mu\text{m}$. This can be explained by the longer time period (8h) of heat treatment of the first sample compared to the treatment of the second one. This long time period might have promoted the growth of the grain size. The temperature of 1200 °C is enough to crystallize the apatite phase of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$, as observed above, but not enough to eliminate the porosity of the material. Variation of the relative densities as a function of the sintering temperature is reported in Table 1.

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

Sintering temperature (°C)	Green pellets (%)	Sintered pellets (%)
1200	40.9	76.3
1300	40.9	97.2

From Table 1, the $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ pellet sintered at 1200 °C showed 76.3 % of relative density. The sample sintered at 1300 °C, a distinct high relative density of 97.2 % theoretical density was achieved. This very dense ceramic could satisfy the application as an electrolyte in IT-SOFC [19]. Published literature [20] has clearly demonstrated that particle size of precursor powder plays a significant influence in the sintering behavior of ceramic materials. In the present study, the sintering activity of the synthesized powder allowed sintering with a dwelling period of 4h, which is much shorter than the conventional or sol gel methods dwelling period. It also allows sintering at a temperature of 1300 °C, which is about 400 °C lower than that which is used in conventional sintering [21]. Tao et al. [17] reported that the relative densities for $\text{La}_{10}\text{Si}_6\text{O}_{27}$ sintered at 1400 °C for 20h and for a three day period have resulted in densification of 69% and 74%, theoretical density respectively. Increasing the sintering temperature to 1500 °C for 22h has resulted in a density of 80% theoretical density. This is not sufficient for obtaining the high electrical property of the sintered ceramic for the IT-SOFC electrolyte application. Table 2 presents the sintering

conditions for fully dense $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ pellet obtained from the proposed modified sol gel process, which allows for a lower sintering temperature and short period time compared with those which have been reported in the literature.

Table 2- Comparison of sintering condition and relative density of sintered $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ pellet synthesized via modified sol gel method with the literature reports

Processing	Sintering condition	Relative density	Reference
Modified sol gel method	1300 °C, 4h	97.2	This study
Conventional solid state reaction	1450 °C, 96h	~95 %	[22]
Conventional solid state reaction	1700 °C	~95 %	[21]
Sol gel process	1500 °C, 10h	90 %	[23]
Molten salt method	1500 °C, 4h	>90%	[24]
Sol gel process	1450 °C, 20h	92 %	[25]

Conclusions

A new fast and low temperature water-based modified sol-gel method for the preparation of apatite-type $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ was presented. Crystalline $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ apatite powders were successfully synthesized by using Na_2SiO_3 as source of Si. The temperature of crystallization of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ apatite phase was 1200 °C. High dense ceramic 97.2% theoretical density was obtained via proposed method by sintering at 1300 at °C for 4h. The main conclusion of present investigation is the TEOS, the usual high cost reagent, may be substituted by a cheap price Na_2SiO_3 , to obtain pure apatite-type lanthanum silicate, $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$.

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