



Facile preparation of apatite-type lanthanum silicate by a new water-based sol–gel process

Chieko Yamagata*, Daniel R. Elias, Mayara R.S. Paiva, Agatha M. Misso, Sonia R.H. Mello Castanho

Nuclear and Energy Research Institute – Instituto de Pesquisas Energéticas e Nucleares – CCTM (Centro de Ciência e Tecnologia de Materiais), São Paulo, Brazil

ARTICLE INFO

Article history:

Received 13 July 2012

Received in revised form 15 February 2013

Accepted 17 February 2013

Available online 27 February 2013

Keywords:

- A. Electronic materials
- A. Ceramics
- B. Chemical synthesis
- B. Sol–gel chemistry
- C. X-ray diffraction

ABSTRACT

In recent years, apatite-type lanthanum silicates ($[\text{Ln}_{10-x}(\text{XO}_4)_6\text{O}_{3-1.5x}]$ (X = Si or Ge)) have been studied for use in SOFC (solid oxide fuel cells), at low temperature (600–800 °C), due to its ionic conductivity which is higher than that of YSZ (Yttrium Stabilized Zirconia) electrolyte. For this reason they are very promising materials as solid electrolyte for SOFCs. Synthesis of functional nanoparticles is a challenge in the nanotechnology. In this work, apatite-type lanthanum silicate nanoparticles were synthesized by a water-based sol–gel process, i.e., sol–gel technique followed by chemical precipitation of lanthanum hydroxide on the gel of the silica. Na_2SiO_3 waste solution was used as silica source. Spherical aerogel silica was prepared by acid catalyzed reaction, followed by precipitation of lanthanum hydroxide to obtain the precursor of apatite-type lanthanum silicate. Powders of apatite-type lanthanum silicate achieved from the precursor were characterized by thermal analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area measurements (BET). The apatite phase was formed at 900 °C.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Researches into apatite-type rare earth silicates, $[\text{Ln}_{10-x}(\text{XO}_4)_6\text{O}_{3-1.5x}]$ (X = Si or Ge), are attracting considerable attention due to their potential technological applications as alternative electrolyte material [1–3] for solid oxide fuel cells (SOFC) in an effort to decrease the high temperatures of operating. This new family of materials [3–5] exhibit higher oxygen ion conductivity at lower temperatures (600–800 °C) [6,7] than the conductivity of traditional YSZ (yttria stabilized zirconia), which normally operates around 1000 °C. In SOFCs, the high temperature of operating might cause problems such as difficulties in cell sealing, which requires expensive materials, resulting in a low life time of the components due to materials degradation. This high temperature might be decreased by either reducing the thickness of the electrolyte or using alternative materials with higher conductivities. Apatite-type compounds, particularly the rare earth silicate system, might be employed as electrolyte in intermediate temperature SOFC (IT-SOFC), which operates at temperatures in range of 600–800 °C. Among these compounds, lanthanum silicates have exhibited the highest ionic conductivity [7]. However, pure apatite-type $\text{La}_{10}(\text{SiO}_4)_6\text{O}_2$ is difficult to obtain

[7,8]. In solid state reactions, the presence of La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$ secondary phases shows that $\text{La}_{10}(\text{SiO}_4)_6\text{O}_2$ is not an equilibrium phase [9] and consequently not stable. $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ might be readily obtained since it is in equilibrium with those secondary phases [9]. Recently, important researches have been performed on this composition of apatite-structure lanthanum silicates, due to its high ionic conductivity at low temperatures ($\sigma = 7.2 \times 10^{-5} \text{ scm}^{-1}$ at 500 °C, and $1.4 \times 10^{-3} \text{ scm}^{-1}$ at 800 °C) [10]. The electrical properties [6,11] might be improved by incorporation of excess La_2O_3 , into apatite structure to form theoretical $\text{La}_{9.33+x}(\text{SiO}_4)_6\text{O}_{2+1.5x}$ ($x > 0$) compositions.

The synthesis of $\text{La}_{10}(\text{SiO}_4)_6\text{O}_2$, from La_2O_3 and SiO_2 by conventionally solid state reactions, requires long time thermal treatment at high temperatures [12]. This method of synthesis presents some disadvantages such as poor control of the morphology and particle size, due to highly required temperatures. Other factor that strongly contributes to the difficulty in obtaining pure $\text{La}_{10}(\text{SiO}_4)_6\text{O}_2$ is the non-homogeneous mixing of precursor oxides. Sol–gel routes might be used to overcome those disadvantages. The sol–gel technique is interesting, for example, it provides a solution based approach to many simple and complex materials [13], allowing more homogeneous distribution of the components. Particularly in the present case, the sol–gel technique provides homogeneous mixture of La_2O_3 and SiO_2 . In addition, the sol–gel routes use lower heat treatments than the conventional solid state reactions method. Previous studies on the synthesis of apatite-type lanthanum silicate have shown that the sol–gel

* Corresponding author. Tel.: +55 11 31339389; fax: +55 11 31339389.
E-mail addresses: yamagata@ipen.br, chiekoyamagata@gmail.com
(C. Yamagata).

method is attractive. Lanthanum silicate powders have been prepared in air at temperatures ranging from 800 to 1500 °C. Tao [14] has reported the synthesis of apatite-type lanthanum silicates from TEOS and La_2O_3 using the sol–gel technique. According to the work, both $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ and $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ apatite-type lanthanum silicates form, when the gel is calcined at 600 °C for 7 h followed by ball-milling stage, and then calcined at 800 °C for 6 h. The lanthanum silicates are not well crystallized when obtained at 800 °C; however, further heating at 1400 °C, pure apatite-type in good crystallization was achieved. C er elier [15] has synthesized $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ nanocrystalline powders from route based on sol–gel process. TEOS and lanthanum hexahydrate nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as starting materials. High density (up to 90%) could be attained after attrition milling step of the powders. He concluded that the starting particles size and the sintering behavior have a great influence on the relative density of the ceramics. C er elier [3] has also studied the effect of several parameters, such as hydrolysis molar ratio ($\text{H}_2\text{O}/\text{SiO}_2$) ratio, volumetric ratio of catalyst to TEOS and silicon concentration, in gel formation. The method allowed the preparation of $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ powders made up of quite uniform particle size (around 100 nm) and specific surface area of $6 \text{ m}^2 \text{ g}^{-1}$ at 1000 °C. Pure oxyapatite-type $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ has been obtained with $\text{H}_2\text{O}/\text{SiO}_2$ mass ratio = 9.4, volumetric ratio of catalyst to TEOS = 2 and silicon concentration = 0.9 mol L^{-1} . Recently, Qingle [16] discussed the influence of pH value in the sol–gel process to obtain apatite-type $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$. Solutions with different pH (from 1 to 5) were prepared, in which the pH was adjusted with ammonia. The sol obtained from pH 2, named sample 2, showed the maximum value of zeta potential and the most stable state and presented the largest specific surface area of $25.23 \text{ m}^2 \text{ g}^{-1}$ and the smallest particle size of 45 nm when the gel was calcined at 600 °C. The apatite phase begins to form at 800 °C, but not well crystallized. The sample calcined at 1000 °C for 4 h confirmed that the single phase of apatite-type structure

$\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ is formed and in good crystallization with specific surface area of $5.53 \text{ m}^2 \text{ g}^{-1}$ and the particle size around 200 nm.

In the present work, a new water-based sol–gel process for synthesis of lanthanum silicate, using Na_2SiO_3 solution as source of silica is described. It focuses synthesis of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ theoretical composition, using two source of silica: TEOS and Na_2SiO_3 solution (an effluent derived from alkali fusion processing of zircon sand) [17]. The obtained product from this new technique, using Na_2SiO_3 solution, was compared to that achieved from typical sol–gel route using TEOS as starting material. Nanocrystalline $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ powders were successfully synthesized by using two starting materials of Si: TEOS and NaSiO_2 . Higher specific surface area ($27.3 \text{ m}^2 \text{ g}^{-1}$ and $34.2 \text{ m}^2 \text{ g}^{-1}$) and lower particle size of the powders (30–40 nm) were obtained compared to results reached in previous studies above mentioned. Crystallization of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ single phase was obtained by calcining the dried precursor gel at 900 °C for 4 h, 100 °C lower than the temperature utilized by the most recent work [16].

2. Experimental

Lanthanum oxide, La_2O_3 (Aldrich 99.9%), and two sources of silica, TEOS (tetraethyl orthosilicate) and Na_2SiO_3 solution [17], an effluent derived from alkali fusion of zircon sand (ZrSiO_4), were used as the starting materials. The steps involved in the obtaining Na_2SiO_3 solution are schematically showed in Fig. 1. The transparent Na_2SiO_3 solution contains approximately 2% SiO_2 and 10% NaOH .

La_2O_3 was previously calcined at 800 °C in order to remove lanthanum hydroxide and/or oxycarbonates and determine the correct amount of this reagent. Calcined La_2O_3 was then dissolved in 6 M HNO_3 to obtain a clear solution, which was used as La precursor solution. $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ was prepared via the usual sol–gel route. A stoichiometric amount of TEOS was mixed with

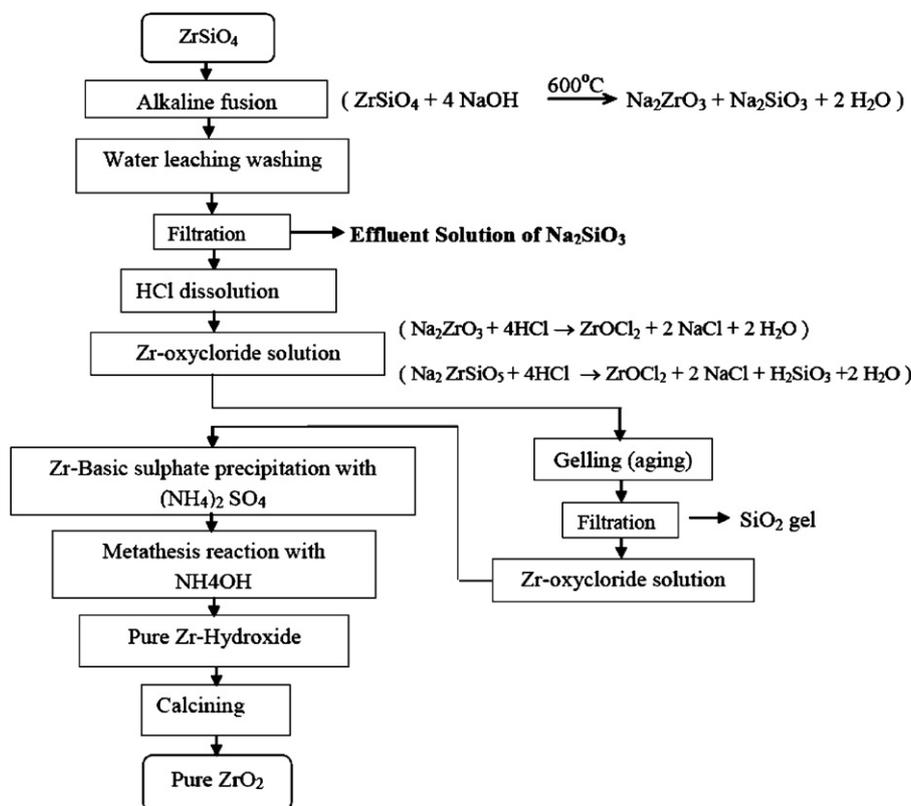


Fig. 1. Flow sheet of pure zirconia powder production by alkali fusion of zircon sand.

ethanol (PA grade) to obtain the precursor solution of Si. Then, the precursor solutions of Si and La were stoichiometrically mixed to achieve the final composition $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$. The resulted mixed solution was added with vigorous and constant stirring to a previously calculate amount of NH_4OH solution (25%) to give a final pH of 10.5. After total addition of the mixed solution, the resulted suspension of mixture was kept with stirring for 5 h to obtain a gel precursor. This gel was filtered and washed with distilled water until pH of 7.0. The washed gel was dried over night at 80°C and calcined to obtain apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ powders. This sample named LSB-956 (lanthanum silicate base catalyzed Si). A second sample was synthesized by using the proposed new water-based sol–gel process, i.e., sol–gel followed by precipitation method. Initially, spherical aerogel silica particles were prepared in HCl medium from Na_2SiO_3 solution, in presence of a surfactant for modification of the wet gel. In a typical synthesis, 3 g of surfactant was dissolved in 10 mL of ethanol and then, 52 mL of 8 M HCl was added to the surfactant dissolved solution, resulting in a clear homogeneous mixture. The solution of silica source (40 mL of Na_2SiO_3 solution) was added at drop wise to the above mixture with constant stirring at room temperature. After complete addition, the mixture was kept at room temperature. After 90 min, a white turbid suspension was obtained. The resulting product was recovered by filtration followed by washing with distilled water up to no Cl^- was identified by AgNO_3 test. To embedding lanthanum in silica gel particles, the washed particles of silica gel were added to the stoichiometric amount (to give $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$) of 6 M HNO_3 in which La_2O_3 was dissolved. The resulted suspension was ultrasonicated for 60 min to disperse the silica particles. Following, quantity previously calculated of 6 M NH_4OH solution to give a final pH of 11, was added to the dispersed mixture with vigorous stirring to precipitate lanthanum hydroxide. The resulted precipitate gel, now containing La and Si, was separated by filtration followed by washing with distilled water and ethanol. The washed precipitate gel was dried over night at 80°C and calcined to obtain apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ powder. This sample named LSA-956 (lanthanum silicate acid catalyzed Si). The obtained powders from both processes were characterized and compared by using thermal analysis (TGA–DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area measurements (BET).

3. Results and discussion

Fig. 2(a) shows the SEM micrographs of silica calcined at 900°C , obtained from NaSiO_2 solution, before precipitation of lanthanum hydroxide. It can be observed in Fig. 2(b), that the particles present porous and soft like. The specific surface area of this sample, determined by BET method was $650\text{ m}^2\text{ g}^{-1}$. This large value of specific surface area is typical of aerogel silica [12]. Efforts to produce aerogels or ambigels led to amorphous oxides after calcination, suggesting those arrangements permit the obtaining silica network that is important to homogeneously disperse the lanthanum salt on its surface [18], since the lanthanum cations do not participate to the formation of the gel network. Any facile low-temperature method for preparing a monophasic metal oxide would require a homogeneous mixing of the component species on an atomic scale [19]. Present work aims to acquire the best possible homogeneous mixing of the precursors of Si and La. In this way, larger surface area of the gel of Si best the homogeneous distribution of La is obtained. Particularly in the present proposed new water-based sol–gel method of synthesis, the obtaining of silica aerogel is primordial. This structure of silica makes easy the dispersion of the lanthanum nitrate salt on the surface of the aerogel, allowing lanthanum cations to be homogeneously distributed along the $-\text{Si}-\text{O}-\text{Si}-$ chains, to posterior precipitation

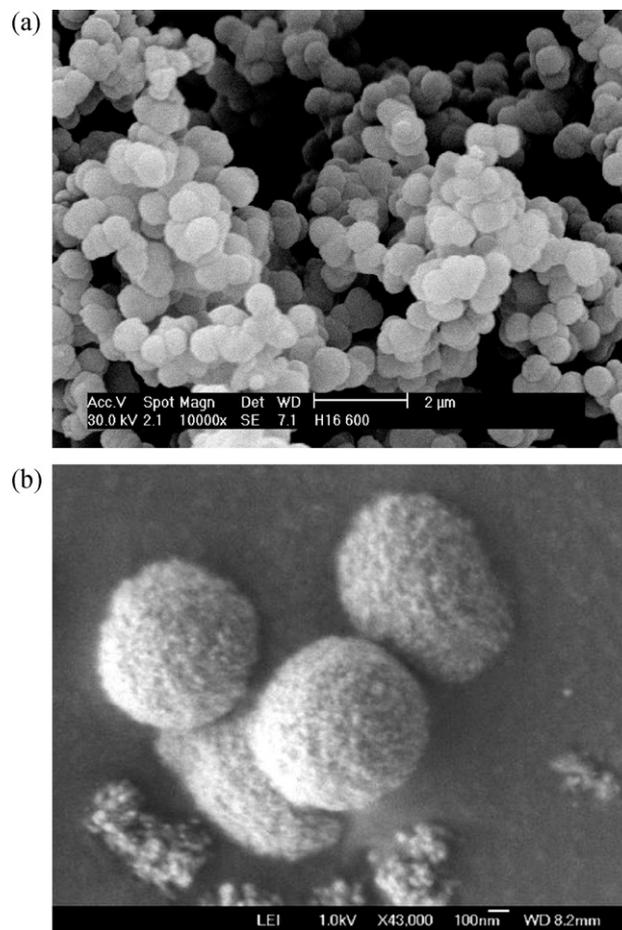


Fig. 2. SEM micrographs of aerogel silica ((a) and (b)) obtained from NaSiO_2 solution, calcined at 900°C . (b) Higher magnification micrograph.

of lanthanum hydroxide with NH_4OH to resulting into $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ by calcining.

In the case of sol–gel method of synthesis using TEOS as silicon starting material, the obtaining of silica aerogel is not required, since the lanthanum and silicon are previous molecular scale homogenized in the precursor mixed solution. When it is added to NH_4OH , the gel of silica and lanthanum hydroxide are practically formed (coprecipitated) at the same time and the homogeneity of lanthanum and silicon, that is very important, is preserved to obtain the final $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ compound.

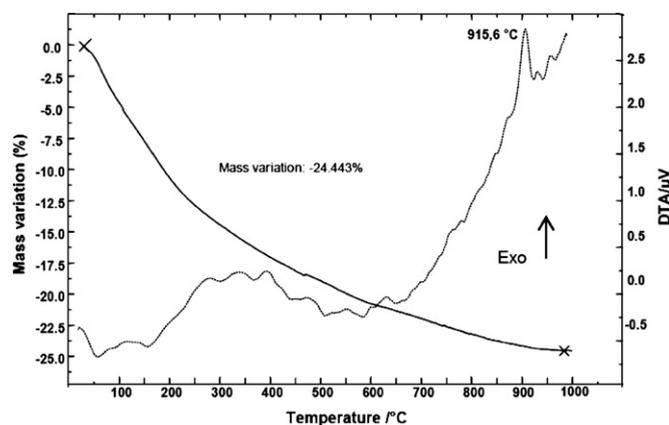


Fig. 3. TGA–DTA curves of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ precursor gel of the sample LSB-956 obtained from TEOS.

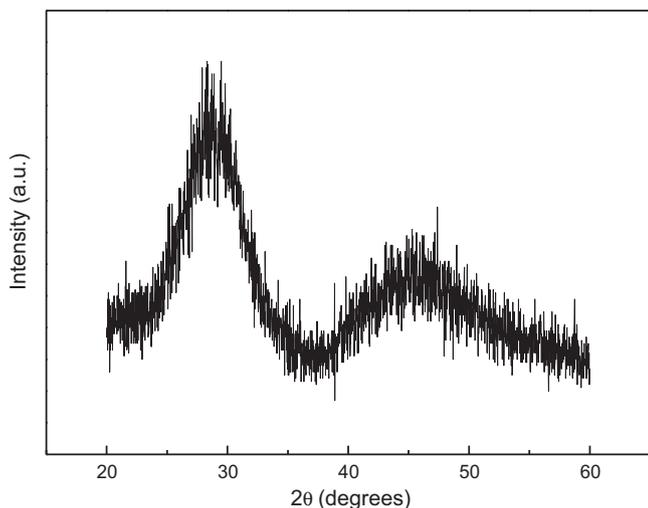


Fig. 4. XRD patterns of the precursor gel of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$, sample LSB-956, obtained from TEOS, calcined at 800 °C for 3 h.

The precursor gel of sample LSB-956 was investigated by thermal analysis as shown in Fig. 3, in order to determine the phase formation and transition temperatures.

The mass variation of 24.443% observed between 25 and 980 °C, in Fig. 3, 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 °C, due to the crystallization or formation of apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ phase, as confirmed by comparison of XRD patterns obtained from the gel thermal treated at 800 and 900 °C, as showed in Figs. 4 and 5 respectively.

From XRD diffraction pattern showed in Fig. 4, it is observed that the sample is amorphous with an indication of the formation of the apatite phase. The sample LSA-956, calcined at 800 °C, also presented peaks free XRD pattern showing amorphous phase at this temperature.

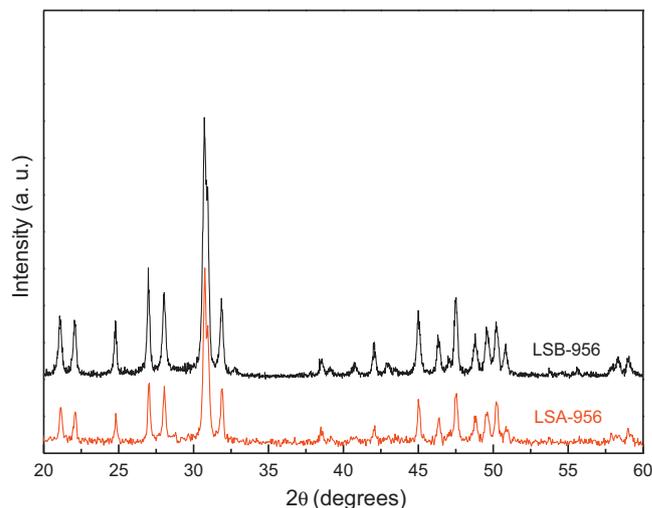


Fig. 5. XRD patterns of the precursor gel of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$, sample LSB-956, obtained from TEOS, calcined at 900 °C for 3 h and the sample LSA-956, obtained from Na_2SiO_3 , calcined at 900 °C for 4 h.

In the XRD pattern showed in Fig. 5 it is observed that the sample LSB-956 is essentially apatite-type crystalline. Presence of $\text{La}(\text{OH})_3$ or La_2SiO_5 crystalline phases could not be observed. The sample LSA-956 also presents analogous XRD patterns of the sample LSB-956 as can be verified in Fig. 5.

The results obtained by BET technique for the samples, LSB-956 and LSA-956 calcined at 900 °C for 3 h and 4 h respectively, presented large specific surface area of 27.3 and 34.2 $\text{m}^2 \text{g}^{-1}$, in that order and particle size around 30–40 nm.

Previous study [3] on the synthesis of apatite-type lanthanum silicate has shown that sintered pellets with relative density of 92% were achieved at 1400 °C, from powders (specific surface area of 6 $\text{m}^2 \text{g}^{-1}$, particle size about 100 nm) synthesized by sol-gel method. This high density was reached by attrition-milling step for 2 h after calcination of powders at 1000 °C for 2 h. Comparing our results of surface area and particle size (27.3 and 34.2 $\text{m}^2 \text{g}^{-1}$,

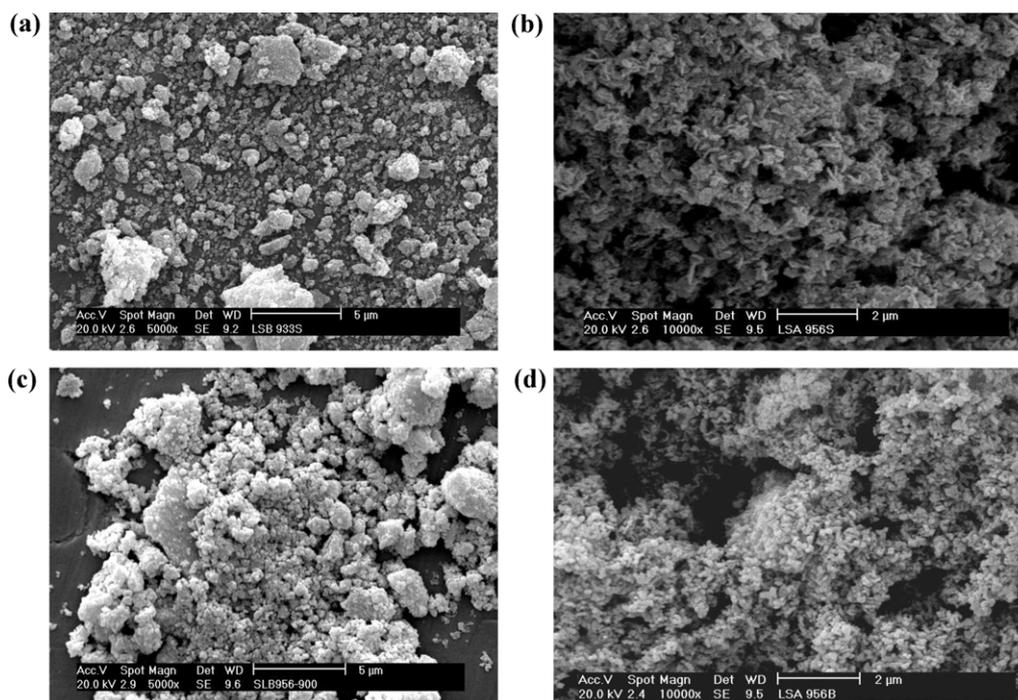


Fig. 6. SEM micrographs of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ sample LSB-956 dried at 80 °C (a) and calcined at 900 °C (c) for 3 h, sample LSA-956 dried at 80 °C (b) and calcined 900 °C (d) for 4 h.

30–40 nm) to results obtained in the above mentioned study (specific surface area of $6 \text{ m}^2 \text{ g}^{-1}$, particle size about 100 nm), it might say that the samples LSB-956 and LSA-956 are promisors to obtain dense ceramics, since large specific surface area and small particle size of the powders promote their reactivity and consequently their good sinterability. However, a milling step of the powders is certainly required before sintering, since the hard particle agglomerates formed in the synthesis are not eliminated during the compaction procedure.

Comparing specific surface area of the samples LSA-956 and LSB-956, the little superior value verified in LSA-956, might be confirmed on the SEM micrographs presented in Fig. 6. In sample LSB-956 (Fig. 6(a) and (c)), the agglomerates are slight hard like compared to those of LSA-956 (Fig. 6(b) and (d)), in which the agglomerates look soft and porous appearance. This might justify a little higher value of the specific surface area reached by the sample LSA-956. Particle size evaluated from specific surface area of the powders, were around 37 and 30 nm for sample LSB-956 and LSA-956, respectively. From Fig. 6 it can be observed that both samples presented similar characteristics of the particle or the agglomerate size.

4. Conclusion

A new fast and low temperature water-based sol–gel method for the preparation of apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ was presented. Nano-crystalline $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ powders were successfully synthesized by using two starting materials of Si: TEOS and Na_2SiO_3 . Particle size of the powder, evaluated by specific surface area ($27.3 \text{ m}^2 \text{ g}^{-1}$ and $34.2 \text{ m}^2 \text{ g}^{-1}$) is between 30 and 40 nm. The temperature of crystallization of $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$ was 900°C . The main conclusion of present investigation is the TEOS, a high cost reagent, may be substituted by a cheap price Na_2SiO_3 , to obtain pure apatite-type lanthanum silicate, $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$. Adding this conclusion, it is important to notice, the Na_2SiO_3 used in the

present work is a waste solution derived from alkali fusion processing of zircon sand. The implement of this solution is environment friendly, since a waste mater was transformed into apatite-type $\text{La}_{9.56}(\text{SiO}_4)_6\text{O}_{2.33}$, a promising material as solid electrolyte for SOFCs.

Acknowledgment

Authors thank to FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), for financial support provided for this research work.

References

- [1] A. Orera, P.R. Slater, Chem. Mater. 22 (2010) 675.
- [2] N.H. Menzler, F. Tiez, J. Mater. Sci. 45 (2010) 3109.
- [3] S. Célérier, C. Laberty, F. Amsart, P. Lenormand, P. Stevens, Ceram. Int. 32 (2006) 271.
- [4] L. Léon-Reina, J.M.P. Vasquez, E. Losilla, M.A.G. Aranda, Dalton Trans. 20 (2007) 2058.
- [5] H. Yoshioka, Chem. Lett. 33 (2004) 392.
- [6] H. Yoshioka, J. Alloys Compd. 408 (2006) 649.
- [7] Y. Masubuchi, M. Higuchi, T. Takeda, S. Kikkawa, J. Alloys Compd. 408 (2006) 641.
- [8] S. Nakayama, M. Sakamoto, J. Eur. Ceram. Soc. 18 (1998) 1413.
- [9] I.A. Bondar, Ceram. Int. 8 (3) (1982) 83.
- [10] L.L. Hench, J.K. West, Chem. Rev. 90 (1990) 33.
- [11] M.M. Vieira, J.C. Oliveira, A. Cavaleiro, B. Trindade, Rev. Adv. Mater. Sci. 18 (2008) 344.
- [12] J.L. Gurav, I. Jung, H. Park, E.S. Kang, D. Nadargi, J. Nanomater. 2010 (2010) 11, Article ID409310.
- [13] A.C. Pierre, Introduction to Sol–gel Processing, Kluwer, Boston, 1998, MA, p. 394.
- [14] S. Tao, J.T.S. Irvine, Mater. Res. Bull. 36 (2001) 1245.
- [15] S. Célérier, C. Laberty-Robert, F. Ansart, C. Calmet, P. Stevens, J. Eur. Ceram. Soc. 25 (2005) 2665.
- [16] S. Qingle, L. Lihua, Z. Yanwei, Z. Hua, J. Wuhan Univ. Technol. – Mater. Sci. Ed. 27 (5) (2012) 841.
- [17] C. Yamagata, J.B. Andrade, V. Ussui, N.B. Lima, J.O.A. Paschoal, Mater. Sci. Forum 591–593 (2008) 771.
- [18] S. Célérier, C. Laberty-Robert, J.W. Long, K.A. Pettigrew, R.M. Stroud, D.R. Rolison, F. Ansart, P. Stevens, Adv. Mater. 18 (2006) 615.
- [19] C.N.R. Rao, J. Gopalakrishnan, Acc. Chem. Res. 20 (1987) 228.