



Synthesis of Oxyapatite $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ Nanocrystals via Solvothermal Method

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Lanthanum silicate ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) nanocrystals with apatite structure for high performance electrolyte of solid oxide fuel cells have been successfully synthesized through a solvothermal process using lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), tetraethyl orthosilicate and acetic acid as starting materials. The as-synthesized lanthanum silicate nanocrystals were structurally characterized by XRD, TEM, HRTEM and FESEM. It has been found that the lanthanum silicate nanocrystals were well-dispersed, quasi-spherical in shape and had a narrow size distribution. Furthermore, the as-synthesized nanoparticles exhibited high sinterability and 95 % of theoretical density was obtained when they were sintered at 1200 °C for 6 h, about 450 °C lower than that derived from conventional solid-state reactions.

Key Words: Nanoparticles, Microstructure, $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$, Solvothermal synthesis.

INTRODUCTION

Rare-earth-based oxyapatites, $\text{La}_{10-x}(\text{SiO}_4)_6\text{O}_{3-1.5x}$ ($x = 0-0.67$), have recently attracted considerable attention as potential electrolyte materials for intermediate and low temperature solid oxide fuel cells due to its low cost, relatively high oxide ion conductivities, moderate thermal expansion and low activation energy¹⁻⁵. The majority of work has been undertaken on preparation of lanthanum silicate ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) via conventional solid-state techniques, which have encountered some troubles. For example, there are some of impurity phases, such as La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$, which tend to degrade the electrical performances of the electrolytes. In addition, lanthanum silicate powders synthesized via solid-state reaction have to be sintered at high temperatures (>1600 °C) for a long time to achieve the desired density, which may result in the reduction of the mechanical properties of the electrolytes, increasing of the energy exhaust and hindering the co-firing of electrolytes with other solid oxide fuel cells elements⁶⁻⁹. The sol-gel route has been proposed to increase reaction rates and to decrease formation temperature of the oxyapatite phase. However, the resulting amorphous oxides has to go through an extra calcination at elevated temperature (> 800 °C) for several hours, in order to obtain the oxyapatite phase¹⁰. Besides, high sintering temperatures (above 1450 °C) are still necessary for densification of the final materials^{11,12}.

By comparison, hydrothermal/solvothermal process offers many advantages over other synthetic methods, such as direct crystallization under hydrothermal condition without sintering,

lower agglomeration, uniform grain size and regular morphology, excellent chemical homogeneity *etc.* Therefore, the synthesis method has been studied in various electrolytes^{13,14}. However, no report is available in literature on the synthesis of nano-sized lanthanum silicate with apatite structure using this method.

In this paper, we report a first successful solvothermal synthesis of highly-monodispersed lanthanum silicate nanocrystals. The synthesis process and sintering properties of the as-prepared lanthanum silicate nanoparticles were also investigated.

EXPERIMENTAL

Solvothermal synthesis of lanthanum silicate: As the starting materials for the formation of lanthanum silicate nanocrystals, the analytical grade lanthanum nitrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], tetraethyl orthosilicate (TEOS), acetic acid and ethanol were used in the present study. They are supplied by Shanghai Lingfeng Chemical Reagent Co., China.

Firstly, appropriate amount of lanthanum nitrate was dissolved in mixed solvents of ethanol (EtOH) and deionized water to give a clear transparent solution after stirring the mixture at room temperature for about 2 h. Then tetraethyl orthosilicate and acetic acid were added into the clear solution and the solution was stirred at room temperature for *ca.* 6 h when hydrolysis of tetraethyl orthosilicate took place and a resultant transparent viscous sol was obtained. The sol transformed into a gel after heating at 80 °C for 4 h. Then the wet

gel was dispersed in a solution of 1,4-butanediol and water. Subsequently, the aqueous solution of KOH was added into the above mixture solution under a vigorous stirring. The mixture was then transferred into a 120 mL Teflon-lined stainless steel autoclave and stirred for 15 min before the autoclave was flushed with N₂ and sealed for solvothermal reactions at 250 °C for 10 h in oil-bath. The whole preparation process was schematically illustrated in Fig. 1.

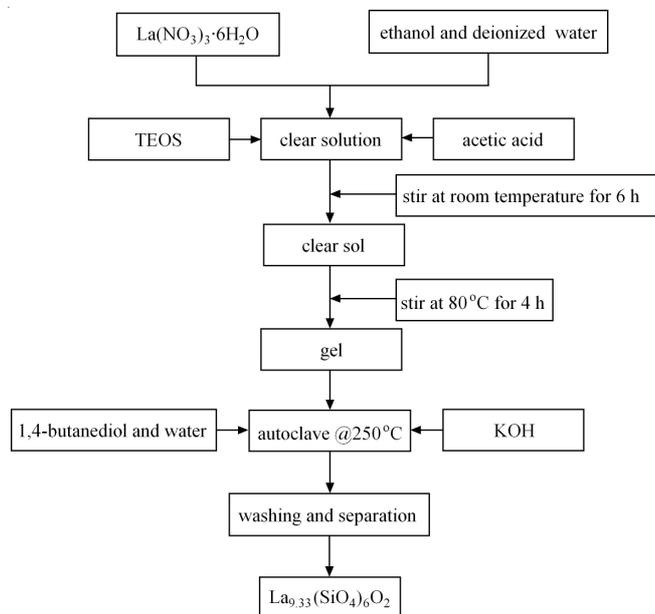


Fig. 1. Schematic flow-chart of the solvothermal synthesis of lanthanum silicate nanocrystals

The as-synthesized lanthanum silicate nanoparticles were mixed with an appropriate amount of 5 wt % polyvinyl alcohols (as the binder) and the granulated powders were uniaxially pressed at a pressure of 300 MPa to form green-specimens. The green pellets were then sintered at 1200 °C for 6 h in air. The densities of the sintered samples were determined using Archimedes method.

Characterizations of lanthanum silicate: The crystalline phase of as-obtained white powders was identified and analyzed by X-ray diffraction (XRD, ARL X'TRA) using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) with a tube power of 40 Kv/35 mA over the 2θ range from 20° to 80° at a scan rate of 2°/min with a goniometric resolution of 0.02° in 2θ . The particle size, morphology of as-obtained nanoparticles and the microstructures of sintered pellets were investigated by TEM/HRTEM (JEM-2100/JEOL) and FESEM (Hitachi S-4800), respectively.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern of the product derived from solvothermal at 250 °C for 10 h. It can be seen that the XRD pattern clearly exhibits a single crystalline phase with a hexagonal apatite structure, which is in good agreement with the JCPDS file 49-443 for La_{9.33}Si₆O₂₆.⁵ The high intensity and well resolved diffraction peaks indicate the high crystallinity of the samples. Moreover, according to the line-broadening calculation by Scherrer's formula, the average size of the lanthanum silicate nanocrystals is about 45 nm.

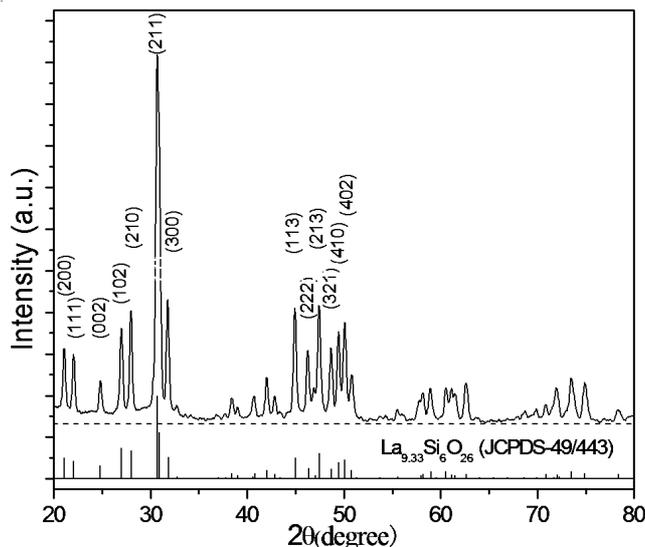


Fig. 2. XRD pattern of the solvothermal product obtained at 250 °C for 10 h

As regards the microstructural features of the solvothermal product, the representative TEM and HRTEM images are presented in Fig. 3. As seen from the photograph (Fig. 3a), the lanthanum silicate nanocrystals are well-dispersed, quasi-spherical in shape and have a narrow size distribution ranging from 30 to 70 nm (Fig. 3b), which gives an average size of 46 nm in a good agreement with the calculated size by XRD line broadening effect. Fig. 3c shows a typical selected area electron diffraction (SAED) pattern for a selected nanoparticle in Fig. 3a, indicating that the nanoparticles are nanosized single crystals. Furthermore, Fig. 3d gives a typical HRTEM image for the lanthanum silicate nanocrystals in Fig. 3a. It can be noted that the lattice fringes are clearly visible, showing a high crystallinity for these nanocrystals and the interplanar spacing of 4.02 and 3.30 Å corresponding to the (111) and (102) planes of hexagonal lanthanum silicate, respectively.

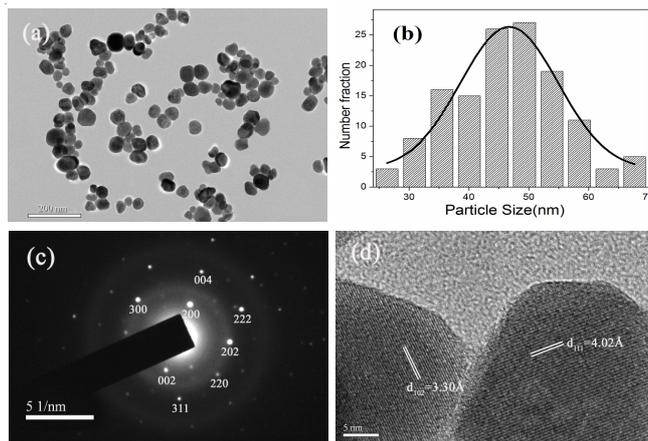


Fig. 3. TEM image of lanthanum silicate nanocrystals (a) synthesized at 250 °C for 10 h and the corresponding particle size distribution (b) of lanthanum silicate nanocrystals, together with a typical SAED pattern (c) and HRTEM image (d) for the nanocrystals in (a), respectively

Fig. 4 shows the typical FESEM micrograph for lanthanum silicate pellets sintered at 1200 °C for 6 h. It can be seen from Fig. 4 that the mean grain size of the sintered body is 0.4 μm

and there are seldom close pores in the sintered samples and all of which are located at the grain boundaries or at the triple points. The satisfactory sintered density was obtained ($> 95\%$) and the powders prepared by solvothermal allow a decrease of $450\text{ }^\circ\text{C}$ of the sintering temperature. By solid-state synthesis, this temperature is $1650\text{ }^\circ\text{C}$ for satisfactory density⁴.

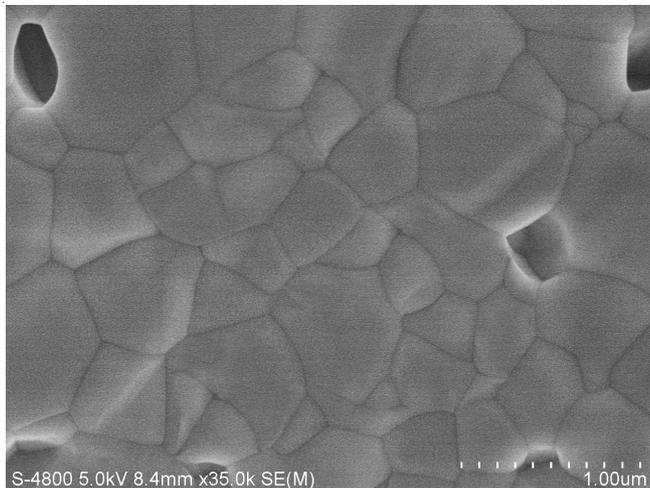


Fig. 4. Typical FESEM cross-section micrograph of lanthanum silicate sintered at $1200\text{ }^\circ\text{C}$ for 6 h

Conclusion

Single phase lanthanum silicate nanocrystals of apatite-type crystal structure were directly synthesized by solvothermal method at $250\text{ }^\circ\text{C}$ for 10 h. Lanthanum silicate nanocrystals were highly-monodispersed, quasi-spherical in shape and had

a narrow size distribution ranging from 30 to 70 nm. The synthesized lanthanum silicate nanoparticles exhibited high sintering activity and the densification temperature is $450\text{ }^\circ\text{C}$ lower than that of powders prepared by solid-state synthesis.

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