Sinterable powder fabrication of lanthanum silicate oxyapatite based on solid-state reaction method

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Sinterable lanthanum silicate oxyapatite (LSO) powders were prepared by the combination of solid-state reaction synthesis and particle size control via planetary ball-milling. We successfully fabricated the LSO ceramics with relative densities exceeding 94% at 1773 K even though it was suggested that the densified LSO ceramics could not be obtained below 1923 K using a powder synthesized by a solid-state reaction. Impurity phases resulting from contamination due to the ball and powder during the planetary ball milling were, in some cases, detected by the X-ray diffraction analysis of the sintered ceramics. The planetary ball-milling conditions were deemed important for the successful fabrication of the sinterable LSO powder.

Key-words : Lanthanum silicate, Oxyapatite, Solid-state reaction, Planetary ball milling, Sinter

1. Introduction

Since Nakayama et al. discovered the oxygen-ion conductivity of lanthanum silicate oxyapatite (LSO), LSO has attracted attention for use as a new solid electrolyte in solid oxide fuel cells (SOFCs). LSO has some advantages compared with yttria stabilized zirconia (YSZ), which is a typical solid electrolyte for SOFCs. For example, LSO has a higher oxygen-ion conductivity than YSZ at temperatures below 873 K. LSO also exhibits a low chemical reactivity to the SOFC cathode materials, lanthanum cobaltite and lanthanum manganite. On the other hand, cobaltite materials, which are expected to have a high cathode activity, react chemically with the YSZ at the SOFC operating temperature, and these reactions render the former unsuitable for use as the SOFC cathode when the latter is employed. However, cobaltite materials are particularly well-suited for cathode materials if LSO is used as the solid electrolyte. Therefore, LSO is favored for the development of an SOFC cell that can be operated at a lower temperature than its YSZ-constructed counterpart.

The numerous difficulties of LSO single-phase synthesis and the low sinterability of LSO compared with the YSZ’s are disadvantageous for SOFC applications. With respect to the LSO synthesis, the pre-heating of La₂O₃ is necessary when the conventional solid-state reaction method is applied using La₂O₃ and SiO₂ as raw materials. The reason is the necessity of removing hydroxide and/or oxhydroxy carbonate, which cause a weighing error, from the La₂O₃ powder. In addition, alcohol must be used as the mixing medium when La₂O₃ is the raw material because La₂O₃ reacts with water. Considering a large amount synthesis, the pre-heating process and use of alcohol become disadvantages of LSO compared with synthesis by other oxygen-ion conductor materials such as YSZ. Even if the LSO single-phase powder is successfully synthesized, sintering temperatures in excess of 1923 K are required for the fabrication of dense LSO ceramics from the synthesized LSO powder. On the other hand, this sintering temperature is far higher than that used for the fabrication of the anode support of the SOFC cell by the co-sintering technique. In this situation, the technology of the cell fabrication process cannot be applied to the LSO electrolyte. Hence, developing an LSO powder fabrication process that can be performed at a maximum sintering temperature of 1773 K is essential.

Low-temperature sinterable LSO powders have been synthesized using several sol–gel methods. The authors have developed another mixing technique of lanthanum hydroxide and amorphous silica using electrostatic interaction between the poly-diallyldimethylammonium chloride and poly-sodium 4-styrenesulfonate modified powders in water. Although the processing procedures was rather complicated, the results indicated that lanthanum hydroxide and water were useful as raw material and mixing medium for LSO synthesis. Considering an industrial application, solid-state reaction processes are preferred owing to the relative simplicity of the synthesis and the large amount of powder that can be produced.

In this study, we attempted to use lanthanum hydroxide instead of La₂O₃ for the preparation of LSO single phase powder in order to simplify the synthesis process and enable the use of a water as mixing medium. In order to confirm the chemical reactivity difference by silica source, quartz-type silica as well as amorphous silica were used, because it was reported that chemical reaction kinetics among lanthanum oxide and amorphous silica was larger than the kinetics among lanthanum oxide and crystalbaltite-type silicate when mechnochemical method was employed.

Furthermore, the effects of the planetary ball-milling on the sinterability, the formed phase, and impurity contamination of the synthesized LSO powder were investigated. Because the LSO particle size control is essential to prepare the sinterable powder.

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2. Experimental

2.1 Synthesis of LSO powder

Lanthanum oxide (La$_2$O$_3$) is typically used as the raw material for lanthanum containing complex oxides. The La$_2$O$_3$ reacts easily with water and carbon dioxide in air, and therefore, a preheat treatment at $\sim$1273 K is necessary before the weighing in order to remove hydroxide and/or hydroxycarbonate. Consequently, water is an unfavorable mixing medium for the La$_2$O$_3$. To overcome this limitation, lanthanum hydroxide [La(OH)$_3$, 99.9% purity, Kojundo Chemical Lab. Co., Ltd., Japan] was selected as the raw material.

Amorphous silica (99.9% purity, Kojundo Chemical Lab. Co., Ltd., Japan) and quartz-type silica (99.9% purity, Kojundo Chemical Lab. Co., Ltd., Japan) were used as raw materials in order to confirm the differences in reactivity between them and La(OH)$_3$. These raw powders are hereafter referred to as a-SiO$_2$ and q-SiO$_2$, respectively.

The nominal LSO composition of La$_{9.50}$(SiO$_4$)$_6$O$_{2.25}$ was based on previously formulated compositions. Accordingly, 9.456 g of La(OH)$_3$, 1.889 g of a-SiO$_2$ or q-SiO$_2$, $\sim$60 g of YSZ balls 5 mm diameter, and 6 cm$^3$ of water were placed in a polyethylene bottle. The raw powders were mixed by a pod mill for 6 h, and the resulting slurry was filtered and dried at 373 K for over 24 h in air. The dried cake was then crushed using an alumina mortar and pestle, and the resulting powder was pressed at 20 MPa into pellets 20 mm in diameter and $\sim$5 mm thick. The pellets were placed on the YSZ setter, and pre-calcinated at 1773 K for 10 h in air. The sintered ceramics using the aforementioned conditions in order to obtain the LSO single phase powder.

The pre-heated samples were then crushed into powder using an alumina mortar and pestle. Hereafter, the pre-heated samples synthesized from La(OH)$_3$ and a-SiO$_2$ are referred to as a-LSO, and those synthesized from La(OH)$_3$ and q-SiO$_2$ are referred to as a q-LSO.

2.2 Particle-size control by planetary ball milling and dense ceramic fabrication

The a-LSO and q-LSO powders were ground by planetary ball milling using a PULYRISETTE7 premium line (FRITSCH, Germany). First, 3 g of the sample powder, 100 g of YSZ balls 1 mm in diameter, and 20 cm$^3$ of water were placed in a ceramic pod made from calcia-stabilized zirconia. The internal volume of the pod was 80 cm$^3$. In order to optimize the grinding conditions, the grinding period was varied from 10 min to 3 h at a fixed rotational speed of 400 rpm. Hereinafter, the a-LSO powder milled for 2 and 3 h are referred to as a-LSO-2h and a-LSO-3h, respectively.

The ground powders were filtered and dried at 373 K for over 24 h in air. The dried cake was crushed using an alumina mortar and pestle, and the a-LSO-2h and a-LSO-3h powders were pressed at 20 MPa into pellets 20 mm in diameter and $\sim$2 mm thick. The pellets were placed on the YSZ setter. The pellets were sintered at 1773 K for 10 h in air. The sintered ceramics using the a-LSO-2h and a-LSO-3h powders are referred to as a-LSO-2h-1773 and a-LSO-3h-1773, respectively.

Regarding the q-LSO, the powder was grounded using the planetary ball mill at 400 rpm for 2 h. This powder is referred to as q-LSO-2h. The q-LSO-2h powder was pressed into pellets and sintered at 1773 K for 10 h in air, similarly to the a-LSO powders. These ceramics are referred to as a q-LSO-2h-1773.

2.3 Characterizations

The phases formed in the samples were determined by powder X-ray diffraction (XRD) analysis (Rint-2500, Rigaku Co., Ltd., Japan) with Bragg-Brentano geometry and Cu K$_\alpha$ radiation at 40 kV and 300 mA using a HOPG graphite monochromator and a Ni filter. The surface morphologies of the powder and ceramic particles were observed by using a field-emission scanning electron microscope (FE-SEM, JSM 6500 M, JEOL Ltd., Japan) operating at an acceleration voltage of 15 kV. In addition, the relative density of the sintered ceramics was evaluated using the Archimedes method.

2.4 Total conductivity measurements

Dense a-LSO and q-LSO ceramics were used for the total conductivity ($\sigma$) measurements. The ceramics were fabricated from the a-LSO-2h, a-LSO-3h, and q-LSO-2h powders. The sintering was performed at 1773 K for 10h in air. The a-LSO-3h-1773 had a rectangular shape 7.8 mm $\times$ 3.3 mm $\times$ 1.2 mm in size, and the a-LSO-2h-1773 and q-LSO-2h-1773 were shaped as a disk with a diameter 15 mm and thickness of 1.1 mm. Platinum was used as the electrode, current collector, and lead wires. The platinum electrode was attached to both surfaces of the sample ceramics using a platinum paste (TR-7907, Tanaka Kikinzoku Kogyo, Japan). The paste-painted samples were heated at 1273 K for 3 min in air in order to remove the organic solvent and the electrode-attached sample was fixed in a handmade cell. The electrodes were attached to two platinum meshes, which were wound around two porous alumina plates. Two platinum wires were connected to each of the platinum meshes; one wire was connected to the current load and the other was connected to the voltage sensing terminals.

The $\sigma$ of the LSO dense ceramics was measured in air at temperatures in the range of 773–1273 K by a 2-probe electrochemical impedance method using a potentiostat-galvanostat (Reference 600M, Gamry Instruments, USA for the a-LSO-3h-1773 and VersaStat 4, Princeton Applied Research, USA for the a-LSO-2h-1773 and q-LSO-2h-1773). Frequencies ranging from 1 MHz to 100 mHz and an amplitude AC voltage of 100 mV were used for the measurements. The bulk resistance cannot be distinguished from that of the grain boundaries by examining the impedance spectra. As such, an apparent bulk resistance, which was evaluated from the dispersed semicircle appearing in the high frequency region, was used for the evaluation of the $\sigma$.

3. Results and discussion

3.1 LSO formation by calcination

The raw powders were weakly aggregated and had particle sizes of $\sim$1 $\mu$m (Fig. 1). The a-SiO$_2$ has a slightly smaller particle size than the a-SiO$_2$, which contained coarse spherical particles larger than 1 $\mu$m.

In addition, a comparison of the XRD patterns (Fig. 2) revealed that the phase formed in the singly pre-calcinated a-LSO powder is different from that in the q-LSO powder. The XRD pattern of the a-LSO consisted of peaks corresponding to the La$_3$SiO$_5$ and oxyapatite phases. However, only the peaks of the oxyapatite phase were observed in the case of the q-LSO powder. As Fig. 3 shows, the oxyapatite single phase in the a-LSO powder formed as a result of the pre-calcination procedures, which were performed twice under identical conditions. These findings suggest that the contamination of the La$_3$SiO$_5$ phase results from the formation of a metastable state.

Regarding the chemical reactivity of La$_2$O$_3$ with a-SiO$_2$ or q-SiO$_2$ to form LSO, an opposite tendency was reported in the case
of LSO mechanochemically synthesized at room temperature; i.e., a-SiO₂ exhibited a higher chemical reactivity than q-SiO₂, and was therefore, deemed preferable for the synthesis of LSO.24) The chemical reactivity of the raw-material particles and pulverizability by planetary ball milling influence the formation of LSO by mechanomechanical synthesis.24) On the other hand, the initial particle size is very important for conventional solid-state reaction methods.29) Figure 1 shows that the particle size of the q-SiO₂ powder used in this study is smaller than that of a-SiO₂. Therefore, the reactivity of the LSO formation by a solid-state reaction, should be strongly governed by the initial particle size of the silica.

3.2 Sinterable powder fabrication by planetary ball milling

The particle morphologies of the a-LSO powder obtained by three pre-calcination procedures and the powders after by planetary ball milling for 10, 30 min, 1, 2, and 3 h are shown in Fig. 4. The non-milled a-LSO (hereinafter referred to as a-LSO-0s) powder is strongly aggregated and has a primary particle size of ~1 μm. The number of large aggregated particles decreases as the milling times increased to 2 h (Fig. 4), and the particle size is apparently constant after 1 h. Comparing the XRD patterns of the a-LSO-0s, a-LSO-1h, and a-LSO-2h reveals the apparent formation of an amorphous phase as well as a decrease in the particle size during milling. These are evidenced by the broadening for all peaks by the LSO crystalline and broad bumps around 2θ = 30° for the a-LSO-1h and a-LSO-2h powders, respectively (Fig. 5). Moreover, the ability to fabricate dense

![Fig. 1. Morphology of raw material powders used in this study observed by FE-SEM. (a) La(OH)₃, (b) amorphous silica (a-SiO₂), and (c) quartz type silica (q-SiO₂).](image-url)
LSO ceramics was confirmed by the a-LSO-2h-1773 and a-LSO-3h-1773 ceramics, which resulted in respective densities of 95.9 and 94.5% relative to the theoretical density. In the case of q-LSO-2h-1773, the relative density was confirmed to be 98.4%. The zirconia contamination in the a-LSO-2h-1773, a-LSO-3h-1773, and q-LSO-2h-1773 during the ball milling was confirmed by the presence of a weak XRD peak that is associated with the La$_2$Zr$_2$O$_7$ and La$_2$Si$_2$O$_7$ phases in Fig. 6.\textsuperscript{30,31}

Although the q-LSO-2h-1773 exhibits a slightly larger grain size ($\approx 2 \mu m$) compared with the a-LSO-2h-1773 and a-LSO-3h-1773 ($\approx 1 \mu m$), as shown in Fig. 7, the grain size of both ceramics are on within the same order.

### 3.3 Total conductivity

The values of $\sigma_t$ for the a-LSO-2h-1773, a-LSO-3h-1773, and q-LSO-2h-1773 are shown in Fig. 8 as a function of the reciprocal temperature. The range of $\sigma_t$ values obtained in previous investigations depicted by the gray area, indicating large differences in the $\sigma_t$ obtained in different studies.\textsuperscript{6} It was found that the values of $\sigma_t$ for the a-LSO-2h-1773, a-LSO-3h-1773, and q-LSO-2h-1773 are within the range of the reported data. The three ceramics employed in this study had nearly identical activation energies of $\approx 0.9$ eV, which is very similar to that of the oxygen-ion conductivity of the LSO ceramics fabricated from sol–gel synthesized powders.\textsuperscript{6,32} Compared with the previous $\sigma_t$ data, the


\[ t \] values exhibit a high reproducibility even using the different raw materials. Although the values of \( t \) for \( \text{a-LSO-2h-1773} \) and \( \text{q-LSO-2h-1773} \) are nearly equal, the \( t \) of \( \text{a-LSO-3h-1773} \) is slightly smaller than those of \( \text{a-LSO-2h-1773} \) and \( \text{q-LSO-2h-1773} \). Because the grain size of \( \text{q-LSO-2h-1773} \) is slightly larger than the grain size of \( \text{a-LSO-2h-1773} \) and \( \text{a-LSO-3h-1773} \), as shown in Fig. 7, it is considered that the size difference does not influence the \( t \) by that order. In addition, we cannot determine a clear dependence of the relative density (95.9\% of \( \text{a-LSO-2h-1773} \), 98.4\% of \( \text{q-LSO-2h-1773} \), and 94.5\% of \( \text{a-LSO-3h-1773} \)) on the values of \( t \).

The XRD patterns of the samples (Fig. 6) revealed that \( \text{La}_2\text{Si}_2\text{O}_7 \) was contained only in the \( \text{a-LSO-3h-1773} \). The \( t \) of \( \text{La}_2\text{Si}_2\text{O}_7 \) is found to be approximately 6 orders smaller than the \( t \) measured in this study. If highly resistive \( \text{La}_2\text{Si}_2\text{O}_7 \) is distributed around the LSO grain, this influence is ideally evaluated as a grain boundary resistance from the impedance spectrum. On the other hand, we cannot separate the grain boundary resistance, owing to the absence of a semicircle shape spectra by the grain boundary impedance. This may be due to very low capacitance around the grain boundary. In this case, it is impossible to separate the bulk and grain boundary resistances by the impedance spectrum. For a detailed clarification of the influence of the \( \text{La}_2\text{Si}_2\text{O}_7 \), grain boundary structure must be observed through further research.

### 4. Conclusion

Sinterable LSO powder was fabricated by the combination of solid-state reaction and planetary ball-milling processes. The LSO single-phase powder was synthesized from two raw material pairs, \( \text{La(OH)}_3 \) and \( \text{a-SiO}_2 \), and \( \text{La(OH)}_3 \) and \( \text{q-SiO}_2 \) by heating at...
1673 K. Although dense LSO ceramics were successfully fabricated at 1773 K using the planetary ball-milled powder, a small amount of the La$_2$Si$_2$O$_7$ and La$_2$Zr$_2$O$_7$ impurity phases were detected after sintering. These results indicate that low sinterability is not a peculiar characteristic of the LSO. In fact, the powder can even be synthesized by the solid-state reaction method, if the particle size can be adequately controlled; i.e., the particle size is an indicator of the sinterability of the LSO. In addition, the total conductivity measured in this work is almost the same as those of previous studies. Future work will include the optimization of the ball milling conditions in order to prevent the formation of impurity phases after the sintering.

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