We synthesize a nanosized lanthanum silicate, La$_{9.33}$Si$_6$O$_{26}$, by means of a hydrothermal method, and then investigate the crystal structure by the Rietveld analysis and the maximum-entropy method using a neutron Bragg profile. In addition, we study electrical conduction properties of the sintered pellet with conductivity measurements under O$_2$ oxidizing and Ar reducing conditions. From these results, it is indicated that the oxyapatite-type lanthanum silicate with oxide-ion conduction can be prepared at 180°C hydrothermally. By using the nanopowder, we prepare a film of the lanthanum silicate via the electrophoretic deposition. As a result, it is demonstrated that a deposited film can be made successfully in an I$_2$-added acetone bath and the thickness obtained in an optimized condition is around 10 μm.

Key-words : Lanthanum silicate, Oxyapatite, Hydrothermal synthesis, Electrophoretic deposition, Ionic conductor

1. Introduction

Lanthanum silicate oxyapatites, which are a family of La$_{9.33}$Si$_6$O$_{26}$, are well known to exhibit excellent oxide-ion conduction at intermediate-temperature range, i.e. around 500°C.[1-5] Therefore, they can be regarded as promising candidates for an electrolyte of the solid oxide fuel cell working at the intermediate temperature (IT-SOFC). When one tries to prepare their dense electrolytes via a conventional solid-state reaction, however, both the material synthesis and the sintering process need extremely high temperature above 1500°C. This fact makes it much difficult to apply the lanthanum silicates for the IT-SOFC. Form such background, it becomes one of hot topics to establish novel synthesis and sintering processes and film preparation methods of the lanthanum silicates. As for the powder-synthesis process, some liquid-based methods, such as a sol–gel method,[6-8] a coprecipitation method,[9-11] an urea-nitrates combustion,[12] a molten-salt synthesis,[13] and a hydrothermal method,[14] succeeded in a preparation of the nanopowder at relatively low temperature. Previous works also applied an alcoxide-hydrolysis method,[15] a plasma spray synthesis,[16-18] a magnetron sputtering,[19,20] a spin coating[21] and an electrophoretic deposition using powder prepared by a sol–gel process,[22] for a film preparation of the lanthanum silicates. In general, however, most of these processes cannot be considered as a simple process, and thus another strategy for manufacturing of the dense film electrolyte is still expected highly at the moment.

In this work, we synthesized La$_{9.33}$Si$_6$O$_{26}$ nanopowder by a hydrothermal method and then characterized the powder from the viewpoint of the cation composition and the crystal structure. In addition, we aimed to prepare a thin film with an easy technique, that is, the electrophoretic deposition (EPD) method using the hydrothermally-synthesized nanopowder. This combination process is proposed here as a novel strategy for the facile preparation of the dense-film electrolyte of the La$_{9.33}$Si$_6$O$_{26}$.

2. Experimental

2.1 Synthesis and characterization

Lanthanum silicate nanopowder was prepared by a hydrothermal method according to literature[14] although the synthesis temperature in our work was lower. 2.47 g of LaCl$_3$·6H$_2$O (Strem Chemicals) and 0.5 g of SiO$_2$ (Merck) were dissolved into 24 mL of 4.8 mol·L$^{-1}$ NaOH aqueous solution. After stirring for 1 h, the solution was transferred to a Teflon-coated stainless-steel vessel with a capacity of 100 mL. A hydrothermal treatment was performed at 180°C for 108 h, and then a precipitate was filtered and washed by distilled water. The obtained powder was identified by an X-ray diffraction measurement (XRD: X’Pert Pro, PANalytical), and the metal composition was evaluated by an inductively-coupled plasma analysis (ICP: ICPE-9000, Shimadzu). The particle morphology was investigated with a scanning electron microscope (SEM: JSM-7600M, JEOL or S-2600N, Hitachi High-Technologies) and the size distribution was estimated by a dynamic light scattering particle size analyzer (FPAR-1000, Otsuka Electronics). In order to study the crystal structure and nuclear-density distributions, a neutron diffraction pattern was measured at room temperature with iMATERIA (BL20) installed at J-PARC, Japan. The pattern recorded at the BS and SE banks was analyzed on the basis of the Rietveld method (Z-Rietveld[23,24]) and the maximum-entropy method (MEM: Z-MEM[25]). The results were visualized by the VESTA program.[26]

For the purpose of electrochemical-property investigation on the hydrothermally-synthesized lanthanum silicate, the obtained powder was pressed into a pellet (ca. 10 mm$^2$ and 1 mm thick-
ness), and then sintered in air at 1000°C for 12 h after a uniaxial pressing. Pt porous electrodes for conductivity measurements were made on both sides of the pellets by firing Pt paste. The Nyquist plots were recorded at 500–800°C by an AC two-probe impedance method with a frequency range from 42 Hz to 5 MHz (3532-50, Hioki), and the conductivities were calculated from total resistances which were estimated from intersects with the horizontal real axis. In the measurements, the atmospheric condition was fixed by using pure O2 or Ar gases.

2.2 Electrophoretic deposition
A film of the lanthanum silicate was prepared by the EPD method. The hydrothermally-obtained powder with a weight of 30 mg was dispersed in acetone (100 mL) by an ultrasonic-wave treatment at 28 kHz for 5 min (B1210J-MTH, Branson). I2 with a weight of 5–30 mg was added as well to form proton and then positively-charged powder in the bath.27)–29) As a substrate for the EPD process, we utilized Ni foil with a fixed area of 5.5 cm² which was masked by Nito fl on adhesive tape. A counter electrode was also Ni foil but its area was larger, i.e., 6.0 cm². These electrodes were placed at a distance of 1.0 cm, and then a DC voltage was applied for 1–3 min with the voltage range from 100 to 250 V (EX-375U2, Takasago). After drying, deposited amounts were calculated by measuring weights of the films in order to optimized EPD condition. A film deposited in the optimized condition was sintered in air at 1000°C for 12 h, and then characterized by XRD and SEM (S-2600N, Hitachi High-Technologies).

3. Results and discussion
3.1 Synthesis and characterization
Figure 1(a) shows an SEM image of as-synthesized powder by the hydrothermal process. It is demonstrated that nanosized powder can be prepared hydrothermally as reported previously.14) From particle-size distribution presented in Fig. 1(b), the number-average size is estimated as ca. 160 nm. An ICP analysis indicated that the cation composition of the sample was La₈.₃₇(¹)Si₅.₉₆(¹)O₂₆ which is almost equal to a typical composition of the lanthanum silicate, i.e., La₉.₃₃Si₆O₂₆.

In order to study the crystal structure, we measured neutron diffraction pattern of the as-synthesized powder, and then analyzed it on the basis of the Rietveld method. The refinement pattern and obtained structure parameters are presented in Fig. 2 and Table 1, respectively. Although a space group of the lanthanum silicate is still under debate,3,30)–32) we assumed it as the most typical one, i.e. P6₃/m.31)–32) without interstitial oxygen. As a result, the refinement could be carried out successfully, and no crystalline impurity phase was detected. Figure 3 depict the refined crystal structure using anisotropic atomic displacement parameters. As well as previous works,3,30)–32) an oxide ion at 2a site tends to be displaced along the c axis from the average position, implying anisotropic oxide-ion conduction through the channel. Nuclear-density distribution estimated by the MEM, presented in this figure as well, suggests the same behavior of the oxide ion. From these results, it can be considered that the hydrothermal process enables us to prepare oxide-ion-conducting lanthanum silicate even below 200°C. For deeper understanding on the oxide-ion behavior, an atomic-configuration analysis by the reverse Monte Carlo simulation3)–34) is in progress, and the result will be reported in the future.

In order to investigate electrical conduction properties of the sample, we sintered the lanthanum silicate nanopowder at 1000°C after a uniaxial pressing. Resistances of the specimen were measured by the AC two-probe impedance method, and Fig. 4(a) shows the Nyquist plots recorded at 600°C under O₂ oxidizing condition as an example. We can observe a single
semicircle apparently. This result means that contributions from the bulk (within grain) and the grain boundary to the resistivity cannot be divided. Therefore, we calculated conductivity of the pellet from total resistivity which was estimated from an intersect of the plot with the horizontal axis. Figure 4(b) presents the conductivities under O2 and Ar conditions as a function of inverted temperature. It is found that the conductivities are essentially independent of partial pressure of oxygen. Such an electrical conduction behavior against ambient condition indicates that the hydrothermally-synthesized lanthanum silicate exhibits predominant oxide-ion conduction at elevated temperature. This result is consistent well with the previous works in which samples were prepared by different processes.35) The conductivities were from 4 × 10^{-6} to 5 × 10^{-4} S·cm^{-1} at 500–800°C, and these values were a little bit lower than reported results.3 This may be because the grain-boundary resistance and/or lower density of the pellet due to the much lower sintering temperature [Fig. 4(c)].

3.2 Electrophoretic deposition

In order to prepare a lanthanum silicate film easily, we focused on the EPD method using the nanosized powder with a nominal composition of La9.33Si6O26 which was synthesized by the hydrothermal process. Firstly, we optimized an I2 concentration in the acetone bath, considering the fact that an appropriate addition of I2 could facilitate powder deposition on a cathode due to proton formation.27) The result is presented in Fig. 5(a). In the experiment, we estimated the deposition amounts with the films before sintering in order to exclude an effect of the substrate oxidation. When I2 was not added into the deposition bath, the powder could not be deposited. As expected, however, it is demonstrated that the I2 addition promotes the deposition of the lanthanum silicate at least up to 0.1 g·L^{-1} of the iodine concentration. Above the concentration, the deposition amount of the sample becomes smaller gradually. This may be due to a decrease of a zeta potential which is caused by a decrease of thickness of the electric double layer in higher I2 concentration.

Table 1. Refined structure parameter of as-synthesized lanthanum silicate (Space group: P63/m). Lattice parameters: a = 9.69251(2) Å and c = 7.18038(2) Å. R-factors: Rwp = 2.37% and Rs = 1.56%.

| Atom | Site | Occupancy | x     | y     | z     | U11/Å² | U22/Å² | U33/Å² | U12/Å² | U13/Å² | U23/Å² |
|------|------|-----------|-------|-------|-------|--------|--------|--------|--------|--------|--------|
| La1  | 4f   | 0.8484(8) | 1/3   | 2/3   | -0.00022(6) |        |        |        |        |        |        |
| La2  | 6h   | 0.9897(5) | 0.23182(4) | -0.01434(4) | 1/4       |        |        |        |        |        |        |
| Si   | 6h   | 1         | 0.40116(7) | 0.37130(6)  | 1/4       |        |        |        |        |        |        |
| O1   | 6h   | 1         | 0.32377(5) | 0.48550(5)  | 1/4       |        |        |        |        |        |        |
| O2   | 6h   | 1         | 0.59390(5) | 0.47010(5)  | 1/4       |        |        |        |        |        |        |
| O3   | 12l  | 1         | 0.34238(4) | 0.25390(4)  | 0.06988(4) |        |        |        |        |        |        |
| O4   | 2a   | 1         | 0       | 0     | 1/4       |        |        |        |        |        |        |

Fig. 3. Refined crystal structure and nuclear-density distribution of the as-synthesized lanthanum silicate (R_{we} = 1.2%).

Fig. 4. (a) Nyquist diagram of the lanthanum silicate sintered at 1000°C. The measurement was performed at 600°C under O2 condition. (b) Conductivities of the sintered specimen under O2 (filled circle) and Ar (open triangle) conditions as a function of inverted temperature. (c) Morphology of the sintered pellet for the electrical conductivity measurements.
bath. Therefore, we regarded 0.1 g·L⁻¹ as an optimal I₂ concentration and fixed this value hereafter.

Figure 5(b) shows the deposition amount of the lanthanum silicate as a function of the deposition voltage. It is found that the deposition amount increased with increasing the voltage up to 200 V. This indicates that the deposition amount, i.e., the film thickness can be controlled by changing the applied voltage. At the higher voltage, however, the amount did not vary essentially. Taking this result into account, we investigated an effect of the deposition time, keeping the deposition voltage at 200 V, and the result is given in Fig. 5(c). In comparison with the voltage, an effect of the deposition time can be regarded as insignificant at least within the investigated time range. This means that one should optimize not the deposition time but the voltage for the purpose of a control of the deposition amount.

Figure 6 shows SEM images of surface and fractured cross-section of the sintered film. These pictures indicates that the lanthanum silicate film is relatively dense and the thickness is about 10 µm which is less than the value in the previous work with the EPD. Although we have to use an appropriate substrate in order to apply the EPD film to IT-SOFC, it can be concluded that our strategy is one of the easy promising ways to manufacture a dense thin film of the lanthanum silicate.

4. Conclusions
Lanthanum silicate nanopowder with a composition of La₉.₃₃3-Si₆O₂₆ was successfully synthesized at 180°C by a hydrothermal method. From a neutron diffraction measurement, it is confirmed that the lanthanum silicate powder has an oxyapatite structure. Conductivity measurements under O₂ and Ar condition indicates oxide-ion conduction in the sintered sample. For a thin-film preparation of the lanthanum silicate, we performed the electrophoretic deposition using the nanopowder in an I₂-added acetone bath. By optimizing the deposition conditions such as an I₂-added amount and an applied voltage, a deposited film with a thickness of about 10 µm can be prepared successfully.

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