Effect of cation doping on ionic conductivity and crystal structure of oxyapatite-type lanthanum silicates

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A B S T R A C T

Crystal structures of oxyapatite-type lanthanum silicate (LSO), $La_{9.667}Si_6O_{26.5}$, and Al- and Mg-doped LSOs; $La_{9.667}(Si_{5.8}Al_{0.2})O_{26.4}$ and $La_{9.667}(Si_{5.5}Mg_{0.5})O_{26.0}$, were refined using synchrotron powder X-ray diffraction (SXRD) data to investigate the origin of enhanced oxide ion (O^{2-}) conducting behavior with Si-site doping. It was found that temperature factors of oxygen atoms largely increased with slight Al- or Mg-doping into the Si-site of LSO. Especially, that for the 2a-site oxygen located on the c axis (O4) was enhanced by doping. In addition, that for the 12i-site oxygen, O3, the constituent of an SiO_4 tetrahedron in the LSO lattice increased with doping anisotropically toward O4. It was suggested that the ionic movement perpendicular to the c axis via SiO_4 tetrahedron was activated by cation (M) doping, and that contributed to the ion conduction in addition to the fast ion channel along c axis.

1. Introduction

Development of high performance solid oxide fuel cells (SOFCs) as clean and sustainable energy systems is expected since they have high conversion efficiency from chemical to electrical energy. The operating temperature of the state-of-the-art SOFC is above 700 °C. This enables energy conversion with high efficiency superior to other energy conversion systems. However, there are some drawbacks such as slow startup/shutdown operations, performance degradation or necessity of high-cost heat-resistant materials due to the high operating temperature, and they are required to be solved. Therefore, reduction in the SOFCs' operating temperature into the intermediate-temperature range (below 600 °C) is required to minimize these problems. For this purpose, a novel solid electrolyte is necessary because of insufficient ionic conductivity of the present solid electrolyte used in SOFCs in this temperature range.

The oxyapatite-type lanthanum silicate ($La_{9.333 + x}Si_6O_{26 + 1.5x}$, LSO), found by Nakayama [1–3], is one of the candidates as an electrolyte material used in the intermediate-temperature SOFCs. We have already developed LSO-based materials with high ionic conductivity by densification, optimizing firing conditions, introducing excess oxygen with

additional La incorporation, and cation doping into its Si-site [4,5]. The Si-site-substituted LSO electrolyte with the optimum composition we developed exhibited superior ionic conductivity to well-known solid electrolyte, yttria stabilized zirconia (YSZ) [4,6]. In addition, its lower activation energy for ionic conduction in the wide temperature range at least down to 500 °C led this material exhibiting higher conductivity than $LaGaO_3$-based solid electrolyte developed by Ishihara [7] at 500 °C. Furthermore, we have shown that this material had high ionic transport number (>0.996 at 800 °C [5]), high chemical stability under the presence of carbon dioxide as well as under the reducing conditions [8], and the doped LSO-based SOFC exhibited good performance with a maximum power density of ca. 0.25 W cm^{-2} at 800 °C [4]. Although it was reported that cation interdiffusion partially blocks the charge transfer reaction at the electrode/electrolyte interface when using cathode materials commonly used in SOFC [9,10], we have succeeded in developing good cathode/electrolyte interface with low area-specific polarization resistance (0.42 Ω cm^2 at 873 K) [11] and anode-supported LSO thin film SOFC [12–14] in order to enhance the SOFC performance further.

However, detailed ionic conducting mechanism of LSO and the reason of the conductivity enhancement with Si-site substitution have not been clarified yet. Effect of substitution on conductivity has been investigated by several groups so far by using structure refinement [15–18], density measurement [19], and theoretical prediction [17,20, 21]. Kendrick et al. [17] suggested that Mg doping on the Si-site led to a local expansion of the oxygen channels for the oxygen-

(pseudo)stoichiometric-type composition, $La_{9.33+2y/3}Si_{6-y}Mg_yO_{26}$. In the same series, Kinoshita et al. [18] found that the La-triangle, which determines oxygen channel size, expanded with Mg-doping into the Si-site. However, to investigate a doping effect, it is preferable to use specimens with the fixed La content since the conductivity of LSO strongly relies upon the La activity [5]. In the present study, change in crystal structure with Al- or Mg-doping into the Si-site was investigated in detail for lanthanum excess-type highly conductive LSO ($x = 0.333$ in $La_{9.333+x}Si_6O_{26+1.5x}$) in order to understand the origin of the improvement in ionic conductivity with the substitution.

2. Experimental

Three composition of LSO electrolytes, $La_{9.667}Si_6O_{26.5}$, $La_{9.667}(Si_{5.8}Al_{0.2})O_{26.4}$, and $La_{9.667}(Si_{5.5}Mg_{0.5})O_{26.0}$ were prepared. In this study, the $x = 0.333$ composition was employed in order to obtain LSO single phase though its conductivity was less than that for the two phases coexistent specimens of $x > 0.333$. For sample preparation, the evaporation-dry method was employed in order to prepare specimens with well-controlled chemical composition. Starting materials were $La(NO_3)_3 \cdot 6H_2O$ (97% purity, Kishida Chemical Co., Ltd.), SiO_2 (0.8 μm particle size, 99.9% purity, Kojundo Chemical Lab. Co., Ltd.), $Al(OH)_3$ (99.0% purity, Kishida Chemical Co., Ltd.), and MgO (99.0% purity, Kishida Chemical Co., Ltd.). The 250 ml of $La(NO_3)_3$ aqueous solution (ca. 0.18 mol dm^{-3}) was prepared at first from $La(NO_3)_3 \cdot 6H_2O$, and the concentration of La^{3+} ion was determined with a chelatometaric titration. After drying and heat treatment at 500 °C for 2 h, resulting powders and weighted powders of SiO_2, $Al(OH)_3$ and MgO were mixed with ethanol, followed by ball milling at 200 rpm for an hour, and calcination at 1400 °C for 10 h. The calcine was pulverized in ethanol for 4 h with a planetary ball milling, and were pelletized into a disk at 57 MPa, and sintered at 1700 °C for 20 h. A density of the specimens was measured with an Archimedes method.

The ionic conductivity was measured with a DC four probe method in air. For the measurements, four platinum wires ($\phi = 0.3$ mm) were attached to the rectangular-shaped specimens ($1.6 \times 0.36 \times 0.18$ cm^3) with platinum paste (Tanaka Kikinzoku, TR-7907), and were baked at 1000 °C for an hour in air. Galvanostat (Hokuto Denko, HA-151) and electrometer (Advantest, R6452E) were used for constant current flowing across the specimen and for voltage measurement between internal electrodes to obtain ionic conductivity.

The SXRD data were collected at room temperature using the Debye–Scherrer camera installed on NIMS beamline BL15XU at SPring-8 [22,23] with $\lambda = 0.65298$ Å with one-dimensional detector Mythen. An imaging plate detector was employed in case of the measurement for $La_{9.667}(Si_{5.8}Mg_{0.5})O_{26.0}$. To obtain X-ray powder diffraction data with sufficiently high quality for the determination of the crystal structure, the samples were ground and sieved several times through a micromesh sieve of 25 μm pore size. Then, uniformly fine particles thus obtained were loaded into a Lindenmann glass capillary with a diameter of 0.1 mm for the measurements. Crystal structure analysis was performed using the Rietveld method with the program RIETAN-FP [24], and electron distribution was analyzed by maximum entropy method (MEM) with PRIMA [25].

3. Results and discussion

3.1. Electrical conductivity

The relative density for the obtained specimens was higher than 96%. Total electrical conductivities (σ) of three specimens measured at 600–1000 °C in air are shown in Fig. 1. The obtained conductivity was regarded as an oxide ion one since this kind of materials exhibits almost pure ionic conductivity as mentioned above. As already reported by Yoshioka [15], the conductivity was found to be enhanced with slight Al- or Mg-doping to the Si-site although nominal excess oxygen content decreased with doping. The σ values obtained are coincident with those
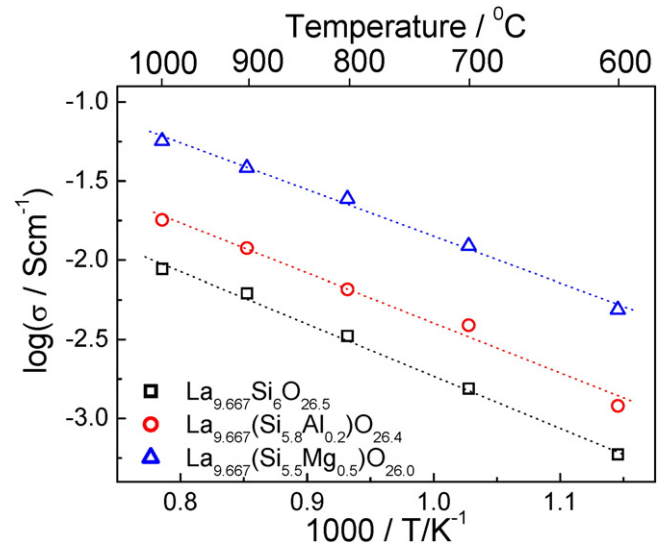

Fig. 1. Temperature dependence of total electrical conductivity of $La_{9.667}Si_6O_{26.5}$, $La_{9.667}(Si_{5.8}Al_{0.2})O_{26.4}$, and $La_{9.667}(Si_{5.5}Mg_{0.5})O_{26.0}$.

for doped LSO with same La content and doping level, presented in literature (e.g. log (σ/S cm^{-1}) = −1.6 and −2.2 at 1073 and 873 K, respectively for the composition of $La_{9.67}(Si_{5.5}Al_{0.5})O_{26.25}$ [26].

A linear relationship was observed in the Arrhenius plot [Eq. (1)] for each specimens between 600 and 1000 °C.

$$\sigma T = Ae^{-\frac{Ea}{RT}} \qquad (1)$$

where A and Ea are the pre-exponential factor and the activation energy, respectively. The evaluated A and Ea values in each case are shown in Table 1. The Ea value decreased with the degree of Si-site substitution, which was coincident with the report by Yoshioka [15]. In our previous paper [4], we suggested that an increase in the ionic conduction perpendicular to the c axis upon Si-site doping contributed to the enhancement in the total conductivity. Fukuda et al. [27] reported that the Ea values of the bulk conductivities for the highly c axis-oriented polycrystalline LSO. The reported Ea values are 0.35 and 0.712 eV (about 34 and 69 kJ mol^{-1}, respectively) for the direction along and perpendicular to the c axis, respectively, whereas Ea value of the total (bulk + grain boundary) conductivity for polycrystalline is about 60–75 kJ mol^{-1} [28]. Hence, the decrease in Ea in polycrystalline specimens by doping is mainly due to the activation of the ionic conducting path perpendicular to the c axis. Since the activation energy for conduction perpendicular to the c axis may be expressed as the linear combination of ion migration enthalpy, ΔH_m and oxygen vacancy formation enthalpy, ΔH_v in SiO_4 tetrahedra, a decrease in the latter contribution by the Si-site substitution may lead to the reduction in the Ea for the overall ion conduction.

On the other hand, the pre-exponential factors, A, evaluated for these specimens increased with doping, and it was suggested that carrier concentration increased with the substitution. Therefore, increase in the conductivity is seemed to be due to the increase in the charge carries as well as the decrease in the Ea for conduction.

Table 1
Activation energy (Ea) and pre-exponential factors (A) in Eq. (1) evaluated for $La_{9.667}Si_6O_{26.5}$, $La_{9.667}(Si_{5.8}Al_{0.2})O_{26.4}$, and $La_{9.667}(Si_{5.5}Mg_{0.5})O_{26.0}$.

Chemical composition	Ea/kJ mol^{-1}	$A/10^4$ S K cm^{-1}
$La_{9.667}Si_6O_{26.5}$	72	1.10
$La_{9.667}(Si_{5.8}Al_{0.2})O_{26.4}$	70	1.80
$La_{9.667}(Si_{5.5}Mg_{0.5})O_{26.0}$	65	3.62