Influence of synthesis route on electrical conduction property, crystal and electronic structures of apatite-type lanthanum silicate

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INTRODUCTION

In recent decades, oxide-ion conductors are expected to be applied for various electrochemical devices, such as sensors and solid oxide fuel cells (SOFC), and play an important role in the field of the solid-state electrochemistry. Among the devices, SOFC has attracted increasing attention because of its high power generation efficiency and low emission of pollutants. The operating temperature of current SOFC is around 1000 ˚C, and thus lowering the operating temperature by 200 ˚C or more is desired to put them into practical use. Since $La_{9.33}Si_6O_{26}$-based oxide-ion conductors have high electric conductivity and low activation energy, these materials become potential candidates for electrolytes of intermediate-temperature SOFC nowadays. In this work, we synthesized the lanthanum silicates by means of a hydrothermal method as well as a conventional solid-state method, and then investigated the effect on conductive properties and crystal structure by differences in synthesis method.

EXPERIMENTAL

$La_{9.33+x}Si_6O_{26+\delta}$ were synthesized by solid-state method and hydrothermal method. In the solid–state method, mixture of La_2O_3, SiO_2 was calcined at 1300 °C for 12 h in air. In the hydrothermal synthesis[1], stoichiometric amounts of $LaCl_3 \cdot 6H_2O$ and SiO_2 were mixed in the 4.2mol/l NaOH aqueous solution. The mixture was stirred for 1 hour at room temperature and then transferred into an autoclave. Synthesis was carried out at 180 °C for 108 h. The powder after washing with distilled water was dried at 100 °C for one day. The product with PVA addition was pressed into a pellet and then sintered at various temperatures. The sample was identified by X-ray diffraction. The composition (La/Si) was tested by inductively coupled plasma spectroscopy (ICP). Powder particle morphology, cross section and surface morphology of bulk samples were observed by scanning electron microscopy (SEM). The density of the sintered pellet was evaluated by the Archimedes method. The conductivity measurements were carried out between 600-900°C by the AC impedance method. Neutron powder diffraction experiments were performed at iMATERIA (J-PARC, Japan). The data were refined using Rietveld technique (Z-code). In order to discuss the effect of synthesis method on crystal and electronic structures, both the samples gained from the solid-state method and the hydrothermal method were also investigated by synchrotron X-ray diffraction, and the data was analyzed by the Rietveld method (REITAN-FP).

RESULTS AND DISCUSSION

As for samples of the solid state method, it was found that the main phase of the samples was attributed to the apatite-type lanthanum silicate. However these samples still contained a secondary phase at least in the synthetic conduction mentioned above.

On the other hand, the powder samples prepared by hydrothermal method had a single phase after heat-treatment at 1100 ˚C(Fig. 1). The analytical composition of $La_{9.33}Si_6O_{26}$ evaluated by ICP analysis was $La_{9.30(1)}Si_{6.02(0)}O_{26+d,}$ and thus essentially equal to the nominal value. From the measurement results of Archimedes method, a relative density of this sample was more than 90 %. Conductivities measured under conditions of oxygen and argon showed similar behavior against temperature, indicating dominant oxygen-ion conduction.

In the Rietveld analysis, two possible space groups ($P6_3/m$ and $P6_3$) were examined. It was found that a space group $P6_3/m$ gave better fit than $P6_3$: R_{wp}=3.12% and 7.46 % for space group $P6_3/m$ and $P6_3$, respectively. From the refined crystal structure of the hydrothermally-synthesized $La_{9.33}Si_6O_{26}$ (Fig. 2), it was found that the oxide ion at the 2a site spread along the c axis and the oxide ions near the c axis, which formed SiO_4, spread towards the 2a site. Therefore it was suggested that oxide ion conducted along the c axis.

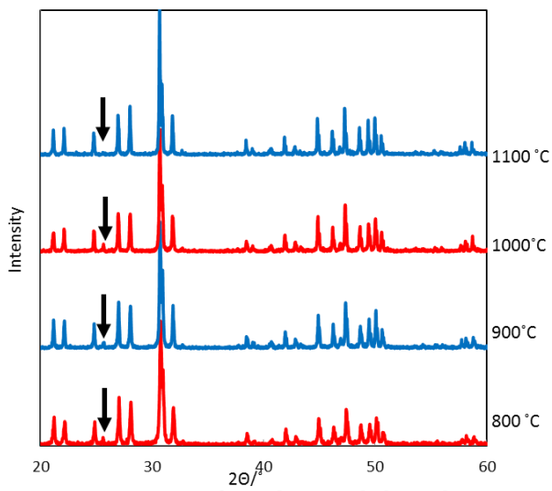

Fig. 1 XRD patterns of powder sample heated at each temperature. Peak positions of an impurity phase are indicated by arrows.

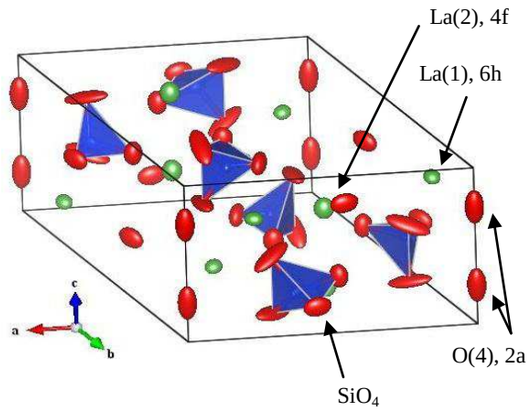

Fig. 2 Refined crystal structure of $La_{9.33}Si_6O_{26}$ (S.G.: $P6_3/m$).

REFERENCES

1)Stanislv Ferdov, Protima Rauwel, ZhiLIn,Rute A Sá Ferreira, Augusto Lopes, J. Solid Sate Chem. , **183**, 2726-2730 (2010).