



Anisotropy of oxide-ion conduction in apatite-type lanthanum silicate

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ABSTRACT

The anisotropy of oxide-ion conduction was clarified for the apatite-type $\text{La}_{9.33+2x}(\text{SiO}_4)_6\text{O}_{2+3x}$ ($0.01 \leq x \leq 0.13$). We synthesized the polycrystalline materials of apatite by the isothermal heating of the sandwich-type $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ diffusion couples at 1873 K for 100 h. The resulting polycrystals were subsequently characterized using optical microscopy, X-ray diffractometry and impedance spectroscopy. The individual *c*-axes of the crystallites were appreciably aligned along the diffusion direction, while their *a*-axes were, around the common *c*-axis direction, oriented randomly. We obtained the impedance spectroscopy data of the polycrystalline electrolyte, the planar electrodes of which were parallel to the common *c*-axis. Thus, the obtained bulk conductivity ($\bar{\sigma}_{\text{bulk}} \perp c$) corresponds to the average value of those perpendicular to the *c*-axis, which steadily increased from 1.6×10^{-5} to 3.8×10^{-4} S/cm with increasing temperature from 623 to 848 K. The bulk conductivity parallel to the *c*-axis ($\bar{\sigma}_{\text{bulk}} \parallel c$) that was determined in a previous study was, when compared at the same temperature, necessarily higher than the corresponding $\bar{\sigma}_{\text{bulk}} \perp c$ value; the magnitude of anisotropy ($\bar{\sigma}_{\text{bulk}} \parallel c / \bar{\sigma}_{\text{bulk}} \perp c$) steadily decreased with increasing temperature from 2.1×10^2 at 623 K to 4.5×10^1 at 823 K. The activation energy of $\bar{\sigma}_{\text{bulk}} \perp c$ was 0.71 eV, which is almost twice that of $\bar{\sigma}_{\text{bulk}} \parallel c$ (0.35 eV).

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1. Introduction

Apatite-type lanthanum silicate, $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ (LSO), is among the most promising oxide-ion conductors for gas-sensing devices and electrolytes for solid oxide fuel cells because of the relatively high conductivity at moderate temperatures as well as at low oxygen partial pressures [1,2]. The crystal structure is highly anisotropic with the space group $P6_3/m$ (optically uniaxial) [3,4]. Nakayama *et al.* have prepared the single crystals of $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$ (RE = Pr, Nd and Sm), which are isostructural with LSO, using floating zone (FZ) method to demonstrate the anisotropy of oxide-ion conduction [5,6]. The conduction mainly occurs along the *c*-axis and hence the conductivity is much higher parallel to the *c*-axis than perpendicular to this direction. Thus, the high performance of oxide-ion conductivity should be also realized for the LSO single crystal along the *c*-axis. However, the FZ method is inapplicable to the growth of this crystal, because it is transparent in infrared light. Recently, the highly *c*-axis-oriented polycrystals of LSO have been successfully prepared by the reactive diffusion between La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$ [7].

When the diffusion couples of $\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ and/or sandwich-type $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ were isothermally heated above 1773 K, the

LSO polycrystals were readily produced in the form of a layer at the original interfacial contact boundaries [7]. The LSO layer was composed of the *c*-axis-elongated prismatic crystallites, the grain-alignment direction of which was almost parallel to the diffusion direction. The formation reaction of LSO is described by



where x ($0.01 \leq x \leq 0.13$ for LSO formed at 1873 K) represents the excess amount of La_2O_3 component in the LSO. The excess oxide ions, which occupy the interstitial sites in the crystal structure, are considered to mediate the high conductivity [8–17]. The highly *c*-axis-oriented LSO polycrystal with $0.09 \leq x \leq 0.13$ showed the bulk apparent conductivity along the *c*-axis ($\bar{\sigma}_{\text{bulk}} \parallel c$) ranging from 2.4×10^{-3} S/cm at 573 K to 2.39×10^{-2} S/cm at 973 K [7]. The empirical activation energy of conduction was 0.35 eV, which is in good agreement with the theoretical migration energy of 0.32 eV evaluated by Béchade *et al.* [8] for the oxide-ion excess LSO. Kim *et al.* [18] analyzed the impedance spectra of randomly grain-oriented $\text{La}_{10.05}(\text{SiO}_4)_6\text{O}_{3.125}$ ($x = 0.375$) polycrystalline material to demonstrate the conduction anisotropy [18]. They derived the two types of activation energies of 0.33 and 0.70 eV; the former was ascribed to the transport along the *c*-axis and the latter perpendicular to this direction.

There is currently much interest in clarifying the diffusion pathways and conduction mechanism of oxide ions in LSO. Béchade *et al.* have

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employed atomic scale computer modeling and simulation techniques to show that the oxide ions conduct along the *c*-axis via a nonlinear pathway [8]. Several researchers have also suggested the nonlinear interstitial transport along the *c*-axis [19–22]. Ali *et al.* have determined the three-dimensional (3D) nuclear density distributions of the doped LSO ($\text{La}_{9.69}(\text{Si}_{5.70}\text{Mg}_{0.30})\text{O}_{26.24}$) at 1831 K using maximum-entropy method-based powder pattern fitting method [12]. The resulting 3D nuclear density distributions suggested that the oxide ions migrate not only along the *c*-axis but also along the direction perpendicular to the *c*-axis. In the present study, we have successfully determined the average value of oxide-ion conductivities along the perpendicular directions to the *c*-axis. The difference in activation energy was manifested between the orientations parallel to the *c*-axis and perpendicular to this direction, which may offer an important clue to clarify the conduction mechanism and pathways of oxide ions in the crystal structure.

2. Experimental

2.1. Material

Two types of powder specimens with different chemical compositions of La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$ were prepared from reagent-grade chemicals of La_2O_3 (99.99%, Mitsuwa Chemicals Co. Ltd., Osaka, Japan) and SiO_2 (99.0%, Kishida Chemical Co. Ltd., Osaka, Japan). Hygroscopic lanthanum oxide was pre-calcined at 1073 K for 30 min in order to remove lanthanum hydroxide and/or oxycarbonate phases to obtain the appropriate amount of La_2O_3 . Individual well-mixed chemicals were heated at 1873 K for 3 h, followed by quenching in air. The reaction products were slightly sintered polycrystalline materials. They were finely ground to obtain fine powder specimens. We prepared sandwich-type diffusion couples of $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$, each of which was made up of one La_2SiO_5 compacted pellet (0.480 g) with the size of ϕ 12 mm \times 0.7 mm and two *m*- $\text{La}_2\text{Si}_2\text{O}_7$ compacted pellets (0.153 g each) with the size of ϕ 12 mm \times 0.3 mm. They were heated at 1873 K for 100 h, followed by cooling to ambient temperature by cutting furnace power.

2.2. Optical microscopy and X-ray diffraction

The annealed couples were cut with a diamond saw to expose sections, the surfaces of which were parallel to the diffusion direction. One part of the cross-sections was subsequently made into thin sections and their microtextures were observed under crossed polars.

The X-ray diffraction (XRD) pattern was taken on the cross-section surface using a diffractometer (model X'Pert PRO Alpha-1, PANalytical B.V., Almelo, The Netherlands) in the Bragg-Brentano geometry, which was equipped with an incident-beam Ge(111) Johansson monochromator to obtain $\text{CuK}\alpha_1$ radiation (45 kV and 40 mA) and a high-speed detector. Other experimental conditions were: continuous scan, experimental 2θ range from 10.0° to 90.0° , 2394 total data points and 15 min total experimental time. The entire experimental diffraction patterns were employed for the Rietveld method [23] to determine the degree of compression or extension of the crystallites due to preferred orientation using a computer program RIETAN-FP [24]. The structural parameters used were those determined by Okudera *et al.* (2005) for $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ [3]. The simulated XRD pattern was generated using this computer program for the apatite polycrystal with a completely random orientation.

2.3. Impedance spectroscopy

One of the annealed couples was ground with 800-grid SiC paper and polished with 1- μm diamond paste to eliminate only the $\text{La}_2\text{Si}_2\text{O}_7$ regions of the disk-shaped specimen. The disc was further cut with a diamond saw along the diffusion direction to obtain the rectangular-shaped electrolyte (Fig. 1). Electrodes were subsequently

prepared by coating the opposite two faces with a platinum paste, which were then heated at 1273 K to decompose the paste and harden the Pt residue. Impedance spectroscopy data were collected in air during heating from 623 to 1073 K using an impedance analyzer (model 3532–80, HIOKI E. E. Co., Nagano, Japan) over the frequency range from 4 Hz to 1 MHz. The impedance spectra were analyzed by a nonlinear least square fitting method using equivalent circuits with a ZView software [25].

3. Results and discussion

3.1. Microtexture of grain-oriented polycrystalline material

The microtexture of the annealed diffusion couple, viewed perpendicular to the diffusion direction (Fig. 2), is essentially the same as those described in a previous study [7]. The former La_2SiO_5 region was completely reacted with the SiO_2 component, which was released from the $\text{La}_2\text{Si}_2\text{O}_7$ regions, to produce the apatite polycrystal in the form of a layer. This layer, termed sublayer I in the previous study, was distinguished from the adjacent two sublayers of apatite by the two marker planes, which are easily recognized by the small voids eventually accumulated along the planes. The latter sublayers, corresponding to the former $\text{La}_2\text{Si}_2\text{O}_7$ regions, were termed II. Since these apatite sublayers I and II in the present study were produced under the same heating temperature and duration as in the previous experiment [7], the chemical variation of the constituent apatite crystals must be represented by $0.06 \leq x \leq 0.13$ for the sublayer I and $0.01 \leq x \leq 0.06$ for the sublayer II of the general formula $\text{La}_{9.33+2x}(\text{SiO}_4)_6\text{O}_{2+3x}$.

Both sublayers I and II were made up of aggregates of prismatic crystallites, which were fairly close to the extinction position under crossed polars (Fig. 2(b)). This implies that the *c*-axis orientations of the crystallites are almost parallel to one another since the apatite crystal is optically uniaxial (i.e., the optical axis is parallel to the crystallographic *c*-axis). The XRD pattern taken on the cross-section surface that is parallel to the diffusion direction showed a marked

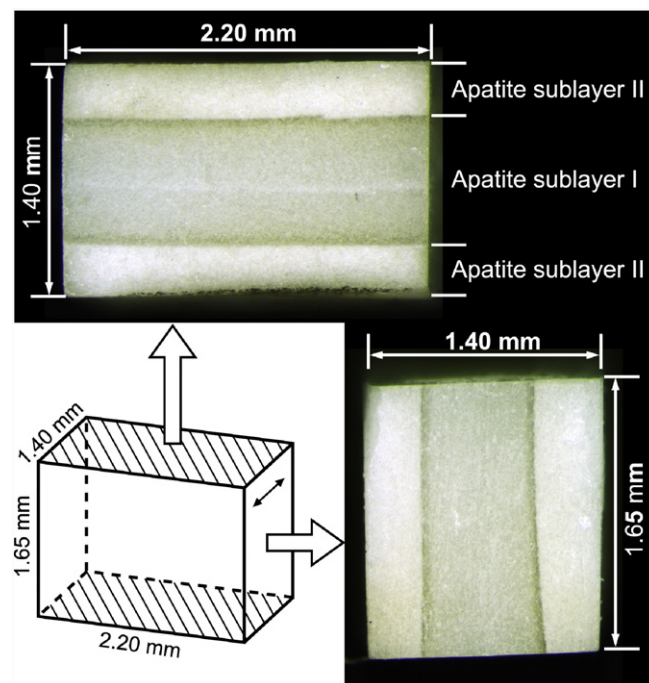


Fig. 1. Optical photographs showing the rectangular electrolyte with the size of ca. 2.20 mm \times 1.65 mm \times 1.40 mm. The double arrow in the schematic figure (left bottom) represents the common *c*-axis direction of the constituent crystallites. The Pt electrodes are prepared on the hatched planes with the area of each electrode (*S*) being ca. 0.02085 cm². The gap separating the electrodes (*L*) is ca. 0.165 cm, and hence the shape factor (*L/S*) of the electrolyte is 7.91 cm⁻¹.

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