Crystal Growth Mechanism of Highly c-Axis-Oriented Apatite-Type Lanthanum Borosilicate Using B₂O₃ Vapor

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ABSTRACT: Apatite-type lanthanum silicate (LSO) exhibits high oxide-ion conductivity and has recently garnered attention as a potential solid electrolyte for high-temperature solid oxide fuel cells and oxygen sensors that operate in the low- and intermediate-temperature ranges (300–500 °C). LSO exhibits anisotropic oxide-ion conduction along with high c-axis-oriented oxide-ion conductivity. To obtain solid electrolytes with high oxide-ion conductivity, a technique for growing crystals oriented along the c-axis is required. For mass production and upscaling, we have thus far focused on the vapor-phase synthesis of c-axis-oriented apatite-type LSO and successfully grew polycrystals of highly c-axis-oriented boron-substituted apatite-type lanthanum silicate (c-LSBO) using B₂O₃ vapor. Here, we investigated the mechanism of c-LSBO crystal growth to determine why the utilization of B₂O₃ vapor resulted in such a strong c-axis crystal orientation. The synthesis of c-LSBO by the B₂O₃ vapor-phase method results in crystal growth accompanied by the diffusion of B₂O₃ supplied from another new compound that formed on the surface of the La₂SiO₅ disk, LaBO₃. In addition, c-LSBO crystals are formed not only by vapor–solid reactions but also by solid–solid and liquid–solid reactions. The increase in the c-axis orientation degree might be due to the increase in the amount of the liquid-phase interface.

INTRODUCTION

Oxide-ion conductors are widely employed as solid electrolytes in electrochemical devices, such as solid oxide fuel cells, oxygen separation membranes, and oxygen sensors for automotive exhaust gases. Yttria-stabilized zirconia (YSZ) is the most commonly employed oxide-ion conductor. However, YSZ requires a temperature of 800 °C or higher to exhibit the oxide-ion conductivity necessary for its application as a solid electrolyte. To reduce the power consumption and the cost of components, electrochemical devices that can operate at temperatures below 600 °C are in demand. To realize this, a novel solid electrolyte must be developed with high oxide-ion conductivity even at low temperatures. Thus far, various oxide-ion-conductive solid electrolyte materials such as cerium oxide, bismuth oxide, bismuth–vanadium oxide, and lanthanum gallate have been proposed.

Apatite-type lanthanum silicate (LSO) exhibits high oxide-ion conductivity below 600 °C and can be potentially applied as a low-temperature solid electrolyte. This material exhibits anisotropic oxide-ion conduction (Figure 1), and the oxide-ion conductivity along the c-axis is one to two orders of magnitude higher than those along the a- and b-axis. Thus far, several synthetic methods to obtain c-axis-oriented apatite have been reported. Among the reports of single-crystal synthesis, those from Nakayama et al. and Fukuda et al. are noticable, whereas Nakayama et al. obtained RE₉.₃₃(SiO₄)₂O₂ (RE = Pr, Nd, and Sm) crystals by the floating-zone method and Fukuda et al. successfully grew (La₉.₂₂Ba₁.₇₈)₂(Si₅.₉₄□₀.₀₆)O₂₆ (where □ denotes a Si site vacancy) crystals using the BaCl₂ flux method. Further, several studies have attempted the synthesis of polycrystalline c-axis-oriented LSO.

Received: October 3, 2020
Accepted: November 20, 2020
Published: December 1, 2020

Figure 1. Crystal structure of apatite-type La₉.₃₃Si₆O₂₆ (PDF number 01-074-9552) drawn using VESTA-3.
Fukuda et al. used the sandwich-type diffusion couple method to promote the reaction between $\text{La}_2\text{Si}_2\text{O}_5$ and $\text{La}_2\text{SiO}_3$ (or $\text{La}_2(\text{Si}_{0.833}\text{Ge}_{0.167})\text{O}_5$) and obtained polycrystalline c-axis-oriented LSO (Lotgering factor, $f_{001} = 0.79−0.90$).\textsuperscript{14−17} Nakayama et al. achieved a c-axis-oriented polycrystalline disk ($f_{001} = 0.481$) through slip-casting under a strong magnetic field.\textsuperscript{18} In addition, Ou et al. synthesized c-axis-oriented LSO ($f_{001} = 0.84$) by arc melting.\textsuperscript{19} The as-obtained c-axis-oriented LSO exhibited higher oxide-ion conductivity than nonoriented LSO. In other words, to achieve high oxide-ion conductivity, LSO crystal orientation along the c-axis is essential, and it is also necessary to develop a crystal orientation technology that is amenable for mass production.

Fukuda et al. proposed the vapor–solid reaction for the synthesis of c-axis-oriented apatite-type LSO polycrystalline ceramics, where $[\text{GeO} + 1/2\text{O}_2]$ or $[\text{SiO} + 1/2\text{O}_2]$ is supplied in the vapor state to a lanthanum silicate ($\text{La}_2\text{SiO}_5$) disk at a temperature of 1400 °C or higher.\textsuperscript{20−22}

\[
(14 + 3y)\text{La}_2\text{Ge}_y\text{O}_{15−y}+ (4 − 3y)[\text{GeO}(g) + 1/2\text{O}_2(g)] \\
\rightarrow 3\text{La}_{9.33+2y}\text{Ge}_y\text{O}_{26+3y}(s) \tag{1}
\]

\[
(14 + 3x)\text{La}_2\text{Si}_x\text{O}_{15−x}+ (4 − 3x − 3y) \]

\[
[\text{SiO}(g) + 1/2\text{O}_2(g)] \\
\rightarrow 3\text{La}_{9.33+2x}\text{Si}_x\text{O}_{26+3x−2y}(s) \tag{2}
\]

where $\square$ denotes a Si site vacancy.

Compared with other methods, such as the diffusion couple method and slip-casting under a strong magnetic field, vapor–solid reactions are more advantageous for upscaling and mass-producing c-axis-oriented LSO. However, the oxide-ion conductivities of the materials prepared by the vapor–solid reaction are $1.04 \times 10^{-2}$ S cm$^{-1}$ at 700 °C and $1.17 \times 10^{-2}$ S cm$^{-1}$ at 800 °C, which are lower than those of single crystals and c-axis-oriented polycrystalline apatite-type LSO formed by the sandwich-type diffusion couple method (1.26 $\times 10^{-2}$ S cm$^{-1}$ at 800 °C). We considered that the low c-axis orientation of these materials ($f_{001} = 0.59−0.70$) leads to the low oxide-ion conductivity. Therefore, a new vapor–solid reaction that can produce highly c-axis-oriented apatite-type LSO should be developed.

Recently, we successfully synthesized a highly c-axis-oriented ($f_{001} = 0.99$) boron-substituted apatite-type lanthanum silicate (c-LSBO) through a vapor–solid reaction using B$_2$O$_3$ as the vapor precursor.\textsuperscript{23} Through this method, we achieved the highest degree of c-axis orientation ever reported for LSO synthesized by vapor-phase methods. The obtained c-LSBO exhibited higher oxide-ion conductivity ($1.6 \times 10^{-2}$ mS cm$^{-1}$ at 400 °C) than both c-axis-oriented LSO synthesized by the diffusion pair method\textsuperscript{14} and YSZ, and an oxygen separation device using c-LSBO as the solid electrolyte showed improved oxygen pumping properties at 600 °C (3.5 mL cm$^{-2}$ min$^{-1}$ under an applied DC voltage of 1.5 V).\textsuperscript{24} In addition, we applied this process to the synthesis of c-axis-oriented Y-doped LSOB and demonstrated the possibility of using it as an electrolyte in a solid electrolyte-type CO$_2$ sensor.\textsuperscript{25} Therefore, highly c-axis-oriented LSO with excellent oxide-ion conductivity is a promising material for developing electrochemical devices that can be operated at low temperatures. However, the mechanism of the high c-axis orientation of c-LSBO has not been clarified. Here, we report a new crystal growth mechanism for the highly c-axis-oriented apatite-type LSO crystals formed from the reaction of $\text{La}_2\text{SiO}_3$ with vaporized B$_2$O$_3$.

## RESULTS AND DISCUSSION

**Preparation of c-Axis-Oriented c-LSBO Polycrystals.** In this study, we first prepared a powder with the chemical composition $\text{La}_2\text{SiO}_3$ by a solid–state reaction between $\text{La}_2\text{O}_3$ and $\text{SiO}_2$. Subsequently, $\text{La}_2\text{SiO}_3$ was molded into disks and subjected to orientational annealing using an electric vertical double furnace (Figure 2) by reacting with B$_2$O$_3$ vapor. In this set-up, B$_2$O$_3$ powder was evaporated in the lower stage and fed to the upper stage where it reacted with solid $\text{La}_2\text{SiO}_3$ disks (see details in the Experimental section). The crystal growth along the c-axis was performed for 40 h with the lower stage at 1300 °C and the upper stage at 1570 °C.

**Highly c-Axis-Oriented c-LSBO Polycrystals.** Figure 3 shows polarized light micrographs of the (a) as-obtained $\text{La}_2\text{SiO}_3$ disk sample before orientational annealing and (c) the disk annealed at a lower-stage temperature of 1300 °C and upper-stage temperature of 1570 °C for 60 h. Upon annealing in the presence of B$_2$O$_3$ vapor, the crystal grains with random shapes turned columnar. Scanning electron microscopy (SEM) images indicate columnar grains in the depth direction (Figure 3d). Rather than just along the thickness, crystal growth is also observed in the lateral direction; the crystal grows as a column from the surface in contact with the B$_2$O$_3$ vapor until the point it makes contact with the crystal grown from the other surface, generating a contact boundary. This result is similar to that obtained with the vapor–solid reaction method using $[\text{GeO} + 1/2\text{O}_2]$.\textsuperscript{20,21} The X-ray diffraction (XRD) pattern of the pulverized LSBO powder in Figure 3f corresponds to the hexagonal apatite structure (PDF number 01-074-9552). The strong 002 and 004 reflection peaks from the surface of c-LSBO indicate that the annealed disk has a c-axis-oriented apatite structure (Figure 3e). The Lotgering factor calculated from the XRD peak intensities is 0.92. The inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis results indicate a cationic composition of $\text{La}/\text{Si}/\text{B} = 9.7:5.3:0.7$ (assuming $\text{Si} + \text{B} = 6.0$). The microarea XRD patterns were collected from the cross section of the obtained sample (Figure 4), wherein the peaks corresponding to the 00l crystal plane of the apatite structure were not detected, indicating that the c-axis-oriented apatite crystals formed uniformly along the depth direction.

### c-Axis-Oriented Crystal Growth.

Figure 5 shows the c-axis orientation degree of samples annealed for 1 h at different...
temperatures between 1350 and 1570 °C in the presence of B$_2$O$_3$ vapor. The c-axis orientation degree is calculated from the total intensity of all reflection peaks and the intensity sum of the 002 and 004 reflection peaks of the XRD intensity. The c-axis orientation degree tends to increase with increasing annealing temperature in the presence of B$_2$O$_3$ vapor. It increases sharply between 1400 and 1500 °C. In addition, comparison of the electron backscatter diffraction (EBSD) images of the c-axis-oriented crystal grains formed at 1400 and 1500 °C indicates that although the c-axis-oriented apatite layer formed at 1400 °C shows preferential orientation in the c-axis direction, some crystal grains are not oriented along the c-axis. The crystal growth direction is also random, and some grains are observed to have grown obliquely. That is, columnar crystals do not grow uniformly in the depth direction at 1400 °C. However, the layer formed at 1500 °C shows more columnar grains than that of the sample annealed at 1400 °C. Next, we investigated the reaction between the B$_2$O$_3$ vapor and La$_2$SiO$_5$ disk. First, Figure 6 shows cross-sectional polarization micrographs and electron probe microanalysis (EPMA) boron mapping images of a sample annealed at 1400 °C for 1 h, 1500 °C for 1 h, and 1570 °C for 1 h. As the temperature is increased, the thicknesses of the B$_2$O$_3$ diffusion layer and oriented layer increased. The thickness of the B$_2$O$_3$ diffusion layer is almost equivalent to that of the c-axis-oriented layer. In other words, c-LSBO is formed by the diffusion of B$_2$O$_3$ into the La$_2$SiO$_5$ disk. B$_2$O$_3$ supplied from the interface diffuses into...
the unreacted part of the La$_2$SiO$_5$ disk through the already formed c-axis oriented layer.

Next, the surfaces of the samples annealed at 1400, 1500, and 1570 °C in the B$_2$O$_3$ vapor for 1 h were analyzed using XRD and EPMA (Figure 7). Aragonite-type LaBO$_3$ \(^{27}\) (PDF number 01-076-1389, space group: Pnma) consisting of La and B layers is formed on the outermost surface of the sample annealed at 1400 °C. In this case, we observed that the vapor-phase method using B$_2$O$_3$ vapor produces a new compound on the outermost surface of the La$_2$SiO$_5$ disk. We consider that LaBO$_3$ is formed from La extracted from La$_2$SiO$_5$, and La$_2$SiO$_5$ that supplied La partially changes to an apatite composition.

\[
(4 - 3x)\text{B}_2\text{O}_3(g) + 18\text{La}_2\text{SiO}_5(s) \\
\rightarrow (8 - 6x)\text{LaBO}_3(s) + 3\text{La}_{9.33+2x}\text{Si}_6\text{O}_{26+3x}(s)
\]

The vapor-phase method using B$_2$O$_3$ vapor differs from the previously reported vapor-phase methods using SiO and GeO$_2$\(^{20-22}\) a new compound, LaBO$_3$, is formed, and c-axis-oriented crystals are grown (Figure 8).

![Figure 6. Polarization micrographs and EPMA B mapping images of the cross sections of samples annealed at (a) 1400, (b) 1500, and (c) 1570 °C for 1 h.](image)

![Figure 7. XRD patterns of the surface and EPMA mapping images of the cross sections of samples annealed at (a) 1400, (b) 1500, and (c) 1570 °C for 1 h.](image)

![Figure 8. LaO$_{1.5}$–SiO$_2$–BO$_{1.5}$ ternary phase diagram.](image)

Here, B$_2$O$_3$ required for the c-axis-oriented crystal growth is supplied from LaBO$_3$ between 1400 and 1500 °C. As there is a continuous supply of B$_2$O$_3$ vapor, the LaBO$_3$ phase does not disappear. Furthermore, the space group of LaBO$_3$ changes from Pnma to P12$_1$/m1 (PDF number 01-073-114) at 1500 °C. At 1570 °C, no layer consisting of La and B exists, and no distinct formation of LaBO$_3$ is observed. The LaBO$_3$ peak corresponding to the space group of P12$_1$/m1 appears with a low intensity in the XRD pattern of the sample annealed at 1570 °C. Alternatively, it might have formed during cooling. Thus, these results suggest that the state of the sample side to which B is supplied differs depending on the annealing temperature. Figure 9 shows SEM images of the sample surfaces annealed at each temperature for 1 h. Annealing in the presence of B$_2$O$_3$ vapor clearly changes the surface state. The sample surface annealed at 1500 °C becomes smooth, suggesting an increase in liquid-phase LaBO$_3$. In contrast, the surface annealed at 1570 °C is not smooth, suggesting that no liquid phase was formed. These results are consistent with La$_2$O$_3$–B$_2$O$_3$ phase diagram proposed by Levin et al.\(^{28}\) The results of the change in the space group and the disappearance of LaBO$_3$ indicate that LaBO$_3$ is formed in the B-rich region of the disk surface. Hence, B$_2$O$_3$ is likely supplied to the disk from the solid–solid phase and liquid–solid phase mixed interface at 1400 °C, the solid–liquid interface at 1400–1500 °C, and the vapor–solid interface at 1500 °C or higher (Figure 10). We consider that the columnar grains grow randomly rather than in the vertical direction when a liquid–solid interface exists locally on an interface containing many solid–solid interfaces. Hence, an increase in the degree of orientation at 1450 °C or higher occurs mostly because of the formation of, and increase in, the liquid–solid interfaces, suggesting that the formation of oriented crystal grains (crystal nucleation) and columnar growth are similar to those achieved with the flux method.\(^{13}\)

**CONCLUSIONS**

For the first time, the c-axis crystal growth mechanism of c-axis-oriented apatite-type LSO crystals grown using B$_2$O$_3$ vapor was clarified. B$_2$O$_3$ supplied in the vapor phase may form a new compound, LaBO$_3$, on the surface of the La$_2$SiO$_5$ disk below...
Germany). The well-mixed powder was heated at 800 °C for 1 h and then sintered at 1650 °C for 3 h, with a diameter of 20 mm, and pressed for 1 min at 600 MPa. The crystal orientation was calculated using the following equations:

\[ f_{00} = \left( \frac{\rho_{00} - \rho_0}{1 - \rho_0} \right) \]

where \( \rho_0 \) represents the value of the randomly oriented sample and can be calculated from the intensity of the XRD peaks in Figure 3e using eq 5:

\[ \rho_0 = \sum I_0(00l) / \sum I_0(hkl) \]  

where \( \Sigma I_0(hkl) \) is the total intensity of all reflection peaks observed in the 2θ range of 20–60° and \( \Sigma I_0(00l) \) is the sum of the intensity of the 002 and 004 peaks.

Subsequently, orientational annealing was performed using an electric vertical double furnace (Figure 2). \( \text{B}_2\text{O}_3 \) powder (99.99%, 100 mg, Kanto Chemical Co., Inc., Tokyo, Japan) was evaporated in the lower stage, and the generated \( \text{B}_2\text{O}_3 \) vapor and solid \( \text{La}_2\text{SiO}_5 \) disks were allowed to react in the upper stages. The lower and upper stages were connected and designed such that the \( \text{B}_2\text{O}_3 \) vapor was fed to the upper stages. A Pt crucible containing 100 mg of \( \text{B}_2\text{O}_3 \) powder was placed in the lower stage, whereas a sintered \( \text{La}_2\text{SiO}_5 \) disk was placed in an Al₂O₃ holder covered with Pt in the upper stage. The lower and upper stages were then heated to 1300 and 1570 °C, respectively, at the rate of 100 °C h⁻¹ and maintained for 40 h. The upper and lower stages were then cooled to the rate of 100 °C h⁻¹. The mechanism of crystal growth along the c-axis was investigated using samples annealed with the lower stage at 1300 °C and upper stage at 1400, 1500, or 1570 °C for 1 h.

### Material Characterization

Polished light microscopy (Olympus BX51, Olympus Corporation, Tokyo, Japan) and field-emission SEM (JSM-7900F, JEOL Ltd. Tokyo, Japan) were conducted to observe the crystal grains in the c-LSBO disks. For polarized light microscopy, we pasted a sample cross section on a glass plate and polished it to a thickness of 100 μm. To observe the crystal-grain orientation, EBSD (Symmetry, Oxford instruments, Oxfordshire, United Kingdom) measurements were performed at an acceleration voltage of 20 kV and sample tilt angle of 70°. The elemental distribution was determined by field-emission EPMA (JXA-8530FPlus, JEOL Ltd. Tokyo, Japan). The grain boundaries were etched by treatment with 3.7% hydrochloric acid for 30 min. The crystal structures of the composite powder and the disk were analyzed by XRD (RINT-TTR III, Rigaku Corporation, Tokyo, Japan) and microarea XRD (SmartLab, Rigaku Corporation, Tokyo, Japan; Cu Ka radiation, \( \lambda = 1.5406 \) Å; 2θ range: 20–60°, scan speed 20° min⁻¹, 50 kV, 300 mA) and microarea XRD (SmartLab, Rigaku Corporation, Tokyo, Japan; Cu Ka radiation, \( \lambda = 1.5406 \) Å; 2θ range: 20–60°, scan speed 5° min⁻¹, 40 kV, 30 mA, measurement area: \( \Phi = 50 \) μm). The crystal orientation was calculated using the following equations:

\[ f_{00i} = \left( \frac{\rho_{00i} - \rho_0}{1 - \rho_0} \right) \]

where \( \rho_0 \) represents the value of the randomly oriented sample and can be calculated from the intensity of the XRD peaks in Figure 3e using eq 5:

\[ \rho_0 = \sum I_0(00l) / \sum I_0(hkl) \]  

where \( \Sigma I_0(hkl) \) is the total intensity of all reflection peaks observed in the 2θ range of 20–60° and \( \Sigma I_0(00l) \) is the sum of the intensity of the 002 and 004 peaks.

\[ \rho_{00i} \] can be calculated from the intensity of the XRD peaks in Figure 3e using eq 6:

\[ \rho_{00i} = \sum I(00l) / \sum I(hkl) \]
The relative density was calculated using the weights and volumes of the samples. The compositions of the synthesized samples were determined by ICP–AES.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the 69th Committee on Materials Processing and Applications, Japan Society for the Promotion of Science (JSPS).

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