Kinetics of reactive diffusion between solid La$_2$GeO$_5$ and gases [GeO + 1/2O$_2$]

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We successfully prepared the polycrystalline lanthanum germanate oxyapatite (LGO) by the reactive diffusion between solid La$_2$GeO$_5$ and gases [GeO + 1/2O$_2$] during isothermal heating at 1573–1723 K for 2–50 h. The reaction products were investigated by polarizing-microscopy for microtexture characterization, Raman spectroscopy for phase identification, and X-ray diffractometry for determination of the (001)$_{LGO}$ texture fractions. The LGO polycrystals were highly c*-axis-oriented, and hence the Lotgering factor $f_{\text{lot}}$ ranged, regardless of annealing temperatures, between 0.94 and 0.99. The thickness ($l$/m) of LGO layer steadily increased with the increase of annealing time ($t$/s) in accordance with a parabolic relationship of $l = [\exp(-1.502 \times 10^6T / -5.233)] \times t^{0.72}$. The growth of LGO layer was predominantly controlled by volume diffusion of GeO$_2$ component, with the activation energy being ca. 125 kJ mol$^{-1}$.

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1. Introduction

Crystal-aligned ceramics are of great interest since they often possess significantly improved performance as compared with randomly grain oriented ones, even though their production methods normally involve complicated processes such as templated grain growth and high-temperature pressing. To overcome the disadvantages of these conventional methods, we have devised a new texturing technique of reactive diffusion, which enables us to readily fabricate highly grain-aligned polycrystalline materials. Actually, we have succeeded in the preparation of grain-oriented polycrystalline lanthanum germanate oxyapatite (LGO) and lanthanum silicate oxyapatite (LSO).4,5

The highly grain-aligned (c*-axis-oriented) polycrystalline LGO has been successfully prepared by the reactive diffusion between solid La$_2$GeO$_5$ and gases [GeO + 1/2O$_2$]. The resulting LGO crystallites were prismatic and aligned along the perpendicular directions to (001)$_{LGO}$. The crystal structure has been characterized by the existence of interstitial oxide ions, which was evidenced by not only single-crystal XRD but also by Raman spectroscopy.4,5 The formation reaction at 1723 K has been described by

$$(14 + 3x)La_2GeO_5 + (4 - 3x)[GeO + 1/2O_2] \rightarrow 3La_{9.33+2x}Ge_6O_{32+3x},$$

where $x$ represents the excess amount of La$_2$O$_3$ component. The LGO with $x \approx 0.17$ (La$_{6.68}$Ge$_{13.52}$) constituted the grain-aligned polycrystals, which was triclinic (space group P1 and $Z = 1$) with unit-cell dimensions of $a = 0.9895$ nm, $b = 0.9906$ nm, $c = 0.7287$ nm, $\alpha = 89.5^\circ$, $\beta = 89.94^\circ$, and $\gamma = 60.1^\circ$.4,5

The highly c*-axis-oriented LSO polycrystal has been readily produced in the form of a layer at the original interfacial contact boundary of the annealed La$_2$SiO$_5$/La$_2$Si$_2$O$_7$ diffusion couple.5 The product LSO layer was demarcated into two adjacent sublayers I and II. The LSO crystals with sublayer I [denoted by LSO(I)] nucleate and grow by the simple reaction of La$_2$SiO$_5$ with SiO$_2$ component that is released from La$_2$Si$_2$O$_7$. On the contrary, the crystals of LSO(II) are principally formed by the loss of SiO$_2$ component from La$_2$Si$_2$O$_7$. For both formation processes of LSO(I) and LSO(II), the diffusion of SiO$_2$ component in LSO plays an important role. In terms of chemical reactions, these processes are described by

$$(14 + 3z)La_2Si_2O_7 + (4 - 7.5z)SiO_2 \rightarrow 3La_{9.33+2z}Si_{6-1.5z}O_{32-5z},$$

and

$$(14 + 3z)La_2Si_2O_7 + (10 + 10.5z)SiO_2 \rightarrow 3La_{9.33+2z}Si_{6-1.5z}O_{32-5z},$$

where $y$ and $z$ represent the amounts of excess La$_2$O$_3$ component and Si deficiency in LSO. The Si deficiency is characteristic of the LSO that coexists with unreacted La$_2$SiO$_3$ of annealed sandwich-type La$_2$Si$_3$O$_7$/La$_2$Si$_2$O$_7$/La$_2$SiO$_3$ diffusion couple.5 During isothermal annealing at 1773–1873 K for 5–100 h, the thickness of each layer increased in proportion to a power function of annealing time, the exponent of which ranged between 0.51 and 0.53.5

Yato and Kajihara have investigated the kinetics of solid-state reactive diffusion in the Au–Ni–Sn system using sandwich-type Sn/(Au–Ni)/Sn diffusion couples, which were isothermally annealed at 433–473 K. After the heart treatment, the layer of AuNi$_2$Sn$_4$ was formed at the interface. The layer thickness increased in proportion to a power function of annealing time. The exponent of the power function ($n$) was close to 0.5 at 453–507 K.
473 K, and 0.7 at 433 K. This implies that, at the higher temperatures, the growth of layer is mainly controlled by the volume diffusion (n = 1/2) of the constituent component, meanwhile the interface reaction (n = 1) also contributes to some extent to the rate determining step at the lower temperature.

In the present study, we succeeded in the preparation of grain-aligned polycrystalline LGO by the solid-gas reactive diffusion at 1573–1723 K. We clarified that the LGO formation was principally controlled by volume diffusion of GeO2 component in the growing LGO layer.

2. Experimental

2.1 Materials

The reagent-grade chemicals of La2O3 (99.99%, Mitsuwa Chemicals Co. Ltd., Osaka, Japan) and GeO2 (99.999%, Mitsuwa Chemicals Co. Ltd., Osaka, Japan) were mixed in molar ratios of [La2O3:GeO2] = [1:1]. The mixture was heated at 1473 K for 4 h, followed by cooling to ambient temperature. The reaction product was a slightly sintered polycrystalline material of La2GeO5, which was thoroughly ground to obtain the fine powder specimen.

Because the sinterability of La2GeO5 powder was poor under ambient pressure, we used a spark plasma sintering method (model SPS-515S, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan) to prepare the densely sintered polycrystalline material. About 5 g of the powder specimen was charged into a graphite die of φ19 mm, compressed at 40 MPa by a press mechanism, heated at 1773 K for 15 min by application of a pulsed current, and then cooled to ambient temperature. The columnar-shaped sintered material (φ19 mm × ca. 3 mm thickness) as obtained was composed exclusively of the La2GeO5 polycrystal with random grain orientation. The crystal-grain size was ca. 5 μm, and the relative density (measured density over theoretical density) was ca. 98%. We cut the columnar sample in round slices using a diamond saw, and prepared a several pieces of disc-shaped specimens (φ19 mm × 1.5–2.7 mm thickness), each of which was subsequently polished with 1 μm diamond paste to obtain the circular thin plate with φ19 mm × 1–2.5 mm thickness.

In our previous study, we generated the [GeO + 1/2O2] gases at 1723 K in air by isothermal heating of GeO2 melt, which was located at the bottom of a Pt crucible.4) The disc-shaped specimen of La2GeO5 was suspended between the bottom and the opening of the crucible using Pt wires. In the present study, we heated the whole assembly, as shown in Fig. 1, at four different temperatures (1573, 1623, 1673, and 1723 K) for five different annealing times (2, 5, 10, 25, and 50 h), and eventually obtained the twenty types of samples. At 1573–1723 K, the GeO2 powder would readily melt to generate [GeO + 1/2O2] gases; the vapor pressure of GeO(gas) under the atmosphere of P(O2) = 0.021 MPa ranges between 5.36 × 10−5 MPa at 1573 K and 1.29 × 10−3 MPa at 1723 K (Fig. 2).8)

2.2 Characterization

The outer shape of each disc-shaped specimen was, before and after the solid–gas reactive diffusion, nearly unchanged. We collected the X-ray diffraction (XRD) data from the flat surface of each sample that was annealed for 50 h using a diffractometer (X’Pert PRO Alpha-I, PANalytical B.V., Almelo, the Netherlands) in the 2θ (Cu Kα1) range from 20.0 to 62.0° (1258 total data points). We used a programmable divergence slit to keep the illuminated length of ca. 10 mm on the flat surface. The texture fractions of [001]LGO planes were determined from the Lotgering factor \( f_{001} \) of the definition of which was given in our previous study.9)

Fig. 1. Schematic assembly drawing (layout) of Pt crucible, GeO2 powder, Pt wire, and disc-shaped specimen of La2GeO5.

Fig. 2. Vapor pressure (P) of GeO(gas) over GeO2(melt) under oxidized atmosphere [P(O2) = 0.021 MPa], calculated using data from NIST-JANAF Thermochemical Tables.9) The P-value at 1573 K is 5.36 × 10−5 MPa [log (P/MPa) = −4.271], and that at 1723 K is 1.29 × 10−3 MPa [log (P/MPa) = −2.891].

We cut each of the disc-shaped specimens along the diffusion direction (perpendicular direction to flat surface) using a diamond saw, and exposed the cross-section. The section surfaces were polished with 1-μm diamond paste, and stuck onto glass slides with epoxy resin. We removed the unnecessary parts of the samples, and prepared the thin sections. The microtextures were observed using a polarizing microscope under crossed polars.

We collected the micro-Raman spectra in the range 100–1000 cm−1 (resolution 1 cm−1) from the reaction products on the thin-section surface. The green line at 532.1 nm of a YAG laser was used for the excitation of spectra (Model NRS-3300, JASCO Co., Tokyo, Japan). The spot size of laser beam (incident power 6 mW) was φ5 μm, and the objective-lens magnification was 100 times. Identification was made by comparison with the reference spectrum, which was collected from La9.68Ge6O26.52.4)

3. Results and discussion

3.1 Microtexture evolution of LGO layer

We confirmed that the reaction products of all samples were LGO, as evidenced by their Raman spectra.3) Each of the spectra showed the overlapping bands ranging from 690 to 800 cm−1, together with a weak band at 648 cm−1 (Fig. S1 and Table S1, Supplementary information). The latter band is peculiar to the
[GeO$_2$]$^{6-}$ polyhedron in LGO, hence the compositional formulas of the present LGO polycrystals would be suitably represented by La$_{9.33+2x}$Ge$_6$O$_{26+3x}$, where $3x$ represents the amount of interstitial oxide ion.$^4$

A series of microtextures of the thin-section specimens demonstrates that, at annealing temperatures of 1573 K (Fig. S2), 1623 K (Fig. S3), 1673 K (Fig. 3), and 1723 K (Fig. S4), the layer thickness of LGO polycrystal steadily increased with increasing annealing time. Each of the XRD patterns, which was obtained from the sample surface, showed an enhancement of intensities with 002 and 004 reflections. Thus, we confirmed that the orientation direction of the LGO crystallites was along the $c^*$ axis. Among the samples with different annealing temperatures, there was no marked difference in orientation degrees. Actually, the $f_{00l}$-values ranged between 0.94 and 0.99 for the specimens annealed for 50 h (Fig. S5). Because both $\alpha$- and $\beta$-angles of the triclinic unit cell are nearly equal to 90°, the prismatic LGO crystal almost shows straight extinction under crossed polars. When one of the vibrational orientations of polarizer or analyzer was nearly perpendicular to the flat surfaces of the disc-shaped specimens, the LGO crystallites were mostly at the extinction position as shown in Fig. 3(f) and Figs. S2(f)–S4(f).

3.2 Growth behavior of LGO layer
The interface boundaries of La$_2$GeO$_5$/LGO were necessarily planar for all samples. Thus, the average thickness ($l$/$m$) of LGO layer can be evaluated by the equation:

$$l = \frac{A}{w}$$

where $A$-value is the total area of LGO layer, and $w$-value is the total length of LGO layer parallel to the interface.$^{11}$ For example, the thickness of LGO layer in Fig. 3(c) was, after annealing at 1673 K for 50 h, ca. $2.80 \times 10^{-4}$ m. Because a plot of [log $l$] vs. [log $t$] gave straight lines as shown in Fig. 4, the $l$-value can be described as a power function of annealing time ($t/\text{s}$) as follows:

$$l = K(t/t_0)^n$$

where $t_0$ is unit time (= 1 s) and $K$ is proportionality coefficients.$^{11}$ We determined the $K$- and exponent $n$-values as a function of annealing temperature ($T/\text{K}$) by the least-squares method, which are summarized in Table 1. Each of the $n$-values with four different temperatures was found to be close to 1/2, which indicates that the thickness of LGO layer increases nearly parabolically with time. Accordingly, the growth of LGO layer must be principally controlled by volume diffusion$^4,11,12$ We plotted the logarithms of $K$ against 1/$T$ (Fig. 5), and found that the temperature dependence of $K$ is well expressed by the equation:

$$\ln K = -\frac{1000}{T} K'$$

![Fig. 4. Thickness $l$ of apatite layer with time after the reactive diffusion at 1573–1723 K for 2–50 h.](image)

![Fig. 5. Proportionality coefficient $K$ of apatite layer with the reciprocal of temperature.](image)

![Table 1. $K$- and $n$-values with annealing temperatures](image)
\[ K = k^0 \exp(-Q/kT) \]

where \(Q\) is the activation energy for the growth of grain-oriented LGO layer, \(k^0\) is the pre-exponential factor, and \(k\) is Boltzmann constant. The \(Q\) and \(k^0\) values were determined from a least-squares method to be \(Q = 125 \pm 20\) kJ mol\(^{-1}\) and \(k^0 = 5.3 \times 10^{-10}\) m.

In accordance with the discussion in our previous study on solid-state reactive diffusion of LSO,\(^{5}\) the growth of LGO layer by the present solid-gas reactive diffusion would also depend on the rate of two processes, which are the diffusion of GeO\(_2\) component to the growing layer interface (volume diffusion process), followed by their incorporation onto the surface of LGO layer (interfacial process). Because the whole reaction rate is generally determined by the slowest step in such successive reactions, the experimentally determined activation energy must refer to this process.\(^{13}\) The growth of LGO layer is diffusion controlled as mentioned previously, hence the \(Q\)-value would correspond to the activation energy of diffusion of GeO\(_2\) component almost along the \(c^*\) direction in LGO. Based on the \(Q\) and \(k^0\)-values derived from Fig. 5, the layer thickness \((l_{\text{LGO}}/m)\) was, as functions of annealing temperature \((T/K)\) and time \((t/s)\), well represented by

\[ l_{\text{LGO}} = \left[\exp(-1.502 \times 10^4/T - 5.233)\right] \times t^{1/2}. \quad (4) \]

Based on Eq. (4), we are able to estimate the thickness of grain-oriented LGO layer at any temperature \((1573 \leq T/K \leq 1723)\) and time \((2 \leq t/h \leq 50)\).

### 3.3 Comparison of formation rates between layers of LGO and LSO

With solid-state reactive diffusion between La\(_2\)SiO\(_5\) and La\(_2\)Si\(_2\)O\(_7\), Fukuda et al. quantitatively clarified the growth behaviors of both LSO(I) and LSO(II) at 1773–1873 K for 5–100 h, and determined the \(Q\)-values, which were \(Q_1 = 198 \pm 30\) kJ mol\(^{-1}\) and \(Q_2 = 198 \pm 27\) kJ mol\(^{-1}\).\(^{5}\) Each of them is ca. 1.6 times larger than the \(Q_{\text{LSO(I)}}\)-value. Furthermore, the \(k^0\)-values \((K^0 = 1.9 \times 10^{-11} \text{m} \text{s}^{-1})\) are more than 25 times larger than that of LGO. The \(n\)-values were slightly larger than 1/2 over the whole temperature range, hence the growth of LSO layer would be controlled mainly by volume diffusion \((n = 1/2)\) and to some extent by interface reaction \((n = 1)\). Each layer thickness is therefore represented by

\[ l_{\text{LSO(I)}} = \left[\exp(-2.378 \times 10^4/T - 1.657)\right] \times t^{1/2}. \quad (5) \]

and

\[ l_{\text{LSO(II)}} = \left[\exp(-2.378 \times 10^4/T - 1.946)\right] \times t^{1/2}. \quad (6) \]

where \(n = 0.52\) (1773 and 1823 K) and \(n = 0.51\) (1873 K) for Eq. (5), and \(n = 0.51\) (1773 and 1873 K) and \(n = 0.53\) (1823 K) for Eq. (6).\(^{5}\) When compared the Eqs. (5) and (6) at the same annealing temperature and time, the \(l_{\text{LSO(I)}}/l_{\text{LSO(II)}}\) ratio ranged between 1.2 (1823 K) and 1.5 (1773 K). Thus, the formation rate of LSO was found to be more than 1.2 times larger for LSO(I) than for LSO(II).

When we focus on the formation reactions as described by the reaction formulas (1)–(5), the layers of LGO and LSO(I) have a high relativity in that both layers grow as the results of incoming fluxes of GeO\(_2\) for the former and SiO\(_2\) for the latter. However, it would be unreasonable to readily compare the Eqs. (4) and (5), because the applicable ranges in temperature are different from each other \([1573 \leq T/K \leq 1723\) for Eq. (4), and \(1723 \leq T/K \leq 1873\) for Eq. (5)]. On the assumption that both equations hold at the intermediate temperatures, we can derive the \(l_{\text{LGO}}\) and \(l_{\text{LSO(I)}}\) values at, for example, 1748 K with \(2 \leq t/h \leq 50\). At that temperature, the calculated \(l_{\text{LGO}}/l_{\text{LSO(I)}}\) ratio ranged between 3.5 \((t = 2)\) and 3.3 \((t = 50)\), where \(n = 0.52\) with \(l_{\text{LSO(II)}}\). Accordingly, as long as we compare the hypothetical rate of layer formation at 1748 K, it was higher for LGO than for LSO(I).

The formation mechanism as well as the growth process of highly grain-oriented polycrystals by reactive diffusion are still uncertain, and should be investigated further. The detailed characterization of the resulting microtextures using, for example, electron backscatter diffraction method\(^{14}\) would enhance our understanding on the one-dimensional growth behavior of the apatite crystallitites.

### 4. Conclusion

The highly \(c^*\)-axis-oriented polycrystalline lanthanum germanate oxyapatite (LGO) was successfully prepared by the reactive diffusion between solid La\(_2\)GeO\(_4\) and gases [GeO + 1/2O\(_2\)] during isothermal heating at 1573–1723 K for 2–50 h. The texture fractions of \([100]_{\text{LGO}}\) planes \((f_{\text{LGO}}\)-values\), after annealing for 50 h, ranged between 0.94 and 0.99. The formation of LGO was found to be principally controlled by the volume diffusion of GeO\(_2\) component in the growing LGO layer, the activation energy of which was ca. 125 kJ mol\(^{-1}\). The layer thickness \((l/m)\) was, as functions of annealing temperature \((T/K)\) and time \((t/s)\), well represented by

\[ l = \left[\exp(-1.502 \times 10^4/T - 5.233)\right] \times t^{1/2}. \]

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Appendix A: Supporting information: Supplementary data associated with this article can be found in the online version.

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