FULL PAPER

Templated grain growth of textured lanthanum silicate oxyapatite ceramics

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We have for the first time fabricated the textured ceramics of doped lanthanum silicate oxyapatite (LSO) by templated grain growth method. Tabular template particles of K₂O- and F-doped LSO with well-developed [001] faces were grown by KF flux method, and aligned in BaO-doped LSO matrix by tape casting. The tapes were punched out into disk-shaped pieces, stacked in two layers, and sintered at 1873 K for 50 h. We obtained a disk-shape K₂O- and BaO-doped LSO polycrystal aligned in the c-axis with small amounts of two types of interstitial materials. The texture fraction of apatite [0 0 1] planes was 0.45. The doped LSO was characterized by the heterogeneous distribution of K₂O, the component of which originated from the template particles, within the crystal grains. The chemical formula of the doped LSO was derived from the average composition to be (La₉.₃₃Ba₀.₆₇O₁₆)₀·₉₇(OSi₅.₈₈O₂₆), where ° denotes vacancies in La and/or Si sites. One type of the interstitial materials was composed mainly of BaO and La₂O₃, and the other was rich in SiO₂. As the temperature increased from 773 to 1023 K, the bulk oxide-ion conductivity (σ) steadily increased from 1.89 × 10⁻⁴ to 2.48 × 10⁻³ S cm⁻¹, with the activation energy of conduction (Ea) being 0.78 eV. The σ-values of randomly oriented polycrystal with the same bulk chemical composition steadily increased from 3.89 × 10⁻⁴ to 4.99 × 10⁻³ S cm⁻¹ with increasing temperature from 773 to 1023 K (Ea = 0.78 eV). When the σ-values were compared at the same temperatures, they were 6.7 (973 K) times higher for the former polycrystal than for the latter. The larger σ-values of the c-axis-aligned polycrystal would be principally induced by the substantially higher oxide-ion conductivity along the c-axis than along the other directions in K₂O- and BaO-doped LSO.

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1. Introduction

Lanthanum silicate oxyapatite (LSO) is one of the most promising materials for electrolytes of solid oxide fuel cells because of its relatively high oxide-ion conductivity at relatively low temperatures and low oxygen partial pressures.¹,²) Since the oxide-ions preferentially conduct along the c-axis in the crystal structure (space group P6₃/m),³) it is required to fabricate the single crystals and/or c-axis-aligned polycrystals for the enhancement of conductivity. The conductivity has been also increased by doping of foreign oxides (e.g. BaO)⁴) and introduction of vacancy in Si site.⁵) Actually, the c-axis-aligned polycrystal of (La₉.₃₃Ba₀.₆₇O₁₆)₀·₉₇(OSi₅.₈₈O₂₆) has demonstrated the superior conductivity to that of (La₉.₃₃O₁·₆₇O₁₆)₀·₉₇(OSi₅.₈₈O₂₆), where ° denotes vacancies in La and/or Si sites.³) These grain-aligned polycrystals, including those of lanthanum germanate oxyapatite, sodium titanogallate, and sodium titanooluminate, have been readily prepared by a reactive diffusion technique, in which the appropriate combinations of diffusion couples are simply heated in air at high temperatures where atomic diffusion occurs.⁶)–¹⁰) Although the methodology itself is quite conventional and therefore suitable for the research phase, this technique is disadvantageous in that the resulting grain-aligned polycrystals are relatively small (normally less than 3 cm in diameter for disc-shaped samples) and in some cases contain significant amounts of microcracks. Thus, in power generation tests aimed at practical use, it is necessary to prepare the large-sized and high-strength crystal-aligned electrolytes.

The templated grain growth (TGG) method¹₁,¹₂) is advantageous over the reactive diffusion technique in that the resulting textured polycrystals are in most cases relatively large in size and include few microcracks. This method requires two types of starting materials; one is the anisotropic template seeds that control texture development (template particles) and the other is the fine-grained source materials (matrix powders). In TGG, the template...
particles are dispersed in the dense matrix compact. Since the sintering environment satisfies the criteria for exaggerated grain growth by Hillert\(^{13}\) as well as the condition for Ostwald ripening, the template particles grow large during the heat treatment.\(^{14}\) Fukuda et al. have successfully grown thin tabular crystals of K\(_2\)O- and F-doped LSO by a KF flux method.\(^{15}\) Because these crystal grains exhibited relatively high aspect ratios with well-developed \{001\} faces, they could be appropriately used for the template particles of the TGG method. However, the matrix powders suitable for the c-axis-aligned polycrystals of doped LSO have not yet been reported so far.

Abnormal grain growth (AGG) is a phenomenon in which certain energetically favorable crystal grains grow rapidly in a fine-grained matrix, resulting in a bimodal grain-size distribution.\(^{16}\) In ceramics, the AGG can lead to the formation of extremely large crystal grains (phenocrysts) in a dense fine-grained matrix. With silica-doped alumina, it has been reported to exhibit undesirable AGG behavior.\(^{17}\) The AGG has been considered to be initiated by a sudden increase in the velocity of grain boundaries, which then exhibit relatively high aspect ratios with well-developed \{001\} faces as the template particles of the AGG.\(^{18}\) Fukuda et al. have successfully applied it as the matrix powder. In ceramics, the AGG can lead to the formation of extremely large crystal grains (phenocrysts) in a dense matrix compact. Since the sintering environment satisfies the criteria for exaggerated grain growth by Hillert\(^{13}\) as well as the condition for Ostwald ripening, the template particles grow large during the heat treatment.\(^{14}\) Fukuda et al. have successfully grown thin tabular crystals of K\(_2\)O- and F-doped LSO by a KF flux method.\(^{15}\) Because these crystal grains exhibited relatively high aspect ratios with well-developed \{001\} faces, they could be appropriately used for the template particles of the TGG method. However, the matrix powders suitable for the c-axis-aligned polycrystals of doped LSO have not yet been reported so far.

We used the tabular single crystals of K\(_2\)O- and F-doped LSO with well-developed \{001\} faces as the template particles.\(^{15}\) The reagent-grade chemicals of La\(_2\)O\(_3\), SiO\(_2\), and KF were mixed in molar ratios of [La\(_2\)O\(_3\):SiO\(_2\):KF] = [1.00:1.29:42.64]. It was heated in Pt crucible with lid at 1173 K for 72 h, then slowly cooled to 1073 K at 1 K/h, and followed by rapid cooling to ambient temperature by cutting furnace power. We washed the overall sample with distilled water to remove the flux material, and obtained the tabular single crystals (up to 160 \(\mu\)m diameter and 2–40 \(\mu\)m thick). We used two types of sieves with different square aperture sizes to select the crystal grains with 45–125 \(\mu\)m diameter, hence the largest size of the tabular crystals was \(\sim 125 \mu\)m diameter and 2–40 \(\mu\)m thick. The template particles as obtained were termed sample 1. The present synthesis and sieving methods were exactly the same with those reported in literature. Thus, the general formula of these tabular single crystals should be [La\(_8\)Ba\(_2\)Si\(_6\)O\(_{26}\)F\(_x\)]\(_{0.092}\)\(_{10}\)\(_{10}[\text{Si}_{5.933}\_{0.242}\_{0.186}\_{1.391}]\_{10}\text{O}_{25.758}\_{1.426}\_{0.243}\_{26}\)\(_{x}\) (0 \(\leq x \leq 0.134)\).\(^{19}\) With the average composition being represented by [La\(_8\)Ba\(_2\)Si\(_6\)O\(_{26}\)F\(_x\)]\(_{0.092}\)\(_{10}\)\(_{10}[\text{Si}_{5.933}\_{0.067}]\_{10}\text{O}_{25.758}\_{0.243}\_{26}\)\(_x\) (0 \(\leq x \leq 0.067)\), the bulk chemical composition of sample 1 was derived from the formula to be 40.71 mol % La\(_2\)O\(_3\), 3.81 mol % K\(_2\)O, 53.31 mol % SiO\(_2\), and 2.17 mol % F.

Beaudet-Savignat et al. have reported the occurrence of AGG for the polycrystalline material of La\(_8\)Ba\(_2\)Si\(_6\)O\(_{26}\).\(^{20}\) In our preliminary experiment as given in the Supplementary Information, the sintered polycrystal with this chemical composition (sample A in Supplementary Information) was accompanied by a small amount of interstitial material (probably liquid state at high temperatures) that was rich in SiO\(_2\) and BaO [Figs. S1(a) and S2]. We anticipated the more predominant occurrence of AGG for the polycrystals with much smaller amounts of coexisting liquid. Such specimens should have the lower concentrations of liquid-forming components of SiO\(_2\) and BaO. Thus, we prepared five types of polycrystals with different concentrations of SiO\(_2\) and BaO (Fig. S1, Table S1) to find the satisfactory chemical composition for AGG to be 33.96 mol % La\(_2\)O\(_3\), 49.79 mol % SiO\(_2\), and 16.25 mol % BaO (sample E in Supplementary Information). The numbers of atoms, based on twenty-six oxygen atoms, were found from the chemical composition to be [La:Si:Ba] = [8.111:5.946:1.941]. We prepared the specimen with this chemical composition from the reagent-grade chemicals of La\(_8\)O\(_3\), SiO\(_2\), and BaCO\(_3\) (99.0 %, Kishida Chemical Co. Ltd., Osaka, Japan). They were mixed in molar ratios of [La\(_8\)O\(_3\):SiO\(_2\):BaCO\(_3\)] = [4.055:5.946:1.941], pressed into pellets (\(9.13 \text{ mm} \times 1 \text{ mm}\), heated in Pt crucible at 1873 K for 1 h, and cooled at ca. 13 K/min to ambient temperature. The slightly sintered material as obtained was ground into a fine ceramic powder (sample 2), which was used as the source material for TGG.
during isothermal heating. The densely sintered specimen thus obtained was termed sample 3.

The samples 1 and 2 in mass % ratio of 20/80 (sample 1/ sample 2) were, together with polyvinyl alcohol (PVA), mixed in hot water (PVA/water of 2/98 in mass % ratio). The mixture was stirred to obtain a slurry of 85 mass % total inorganic solids. We obtained a tape with 160 µm thick by slurry casting on a glass surface at 75 mm/s with a blade opening of 600 µm, and drying under ambient condition. These tapes were punched out into disk-shaped pieces of 18.0 mm diameter, stacked in two layers, and pressed uniaxially at 20 MPa to obtain a double-layered green body. The bulk chemical composition of inorganic solids was, based on the chemical compositions of samples 1 and 2 and their mixed ratios of 20/80 in mass %, determined from calculation to be 35.29 mol % La2O3, 0.75 mol % K2O, 13.05 mol % BaO, 50.48 mol % SiO2, and 0.43 mol % F. The disk-shaped green body was heated up to 773 K at 0.52 K/min in air to burn out the binder, and subsequently sintered at 1873 K for 50 h. The sintered polycrystal as obtained was termed sample 4.

We ground the mixed samples 1 and 2 with the mass % ratio of 20/80 into a fine powder, homogeneously mixed, pressed into pellets (φ10 mm × 1 mm), heated at 1873 K for 2 h, and quenched in air to prepare the densely sintered polycrystalline material with random grain orientation (sample 5). The relative density (measured density over theoretical density) of the disk-shaped specimen was ca. 92 %. Thus, the bulk chemical composition as well as the relative density were almost identical to those of sample 4.

We as a result prepared the five types of samples 1–5. Their bulk chemical compositions (mol %) consisting of only the inorganic components are summarized in Table S2. With samples 4 and 5, the F component was almost completely evaporated and the K2O component was partially volatilized after the main heat treatment at 1873 K for 50 h.

2.2 Characterization

A part of sample 3 was ground into a fine powder, and investigated by an X-ray powder diffractometer (XRD, 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) Johannson monochromator to obtain CuKα1 radiation. The other part of the sample 3 was made into thin section. The section surface was polished using a #1500 emery paper, and mirror finished by buff polishing. The microtexture was observed using a polarizing microscope under crossed polars. Concentration distribution maps for BaO, La2O3, and SiO2 were obtained on the polished surface using an electron probe micro-analyzer (EPMA, model JXA-8900L, JEOL, Tokyo, Japan). The analysis area of the maps was 1600 µm × 1600 µm (380 × 380 pixels). The accelerating voltage, probe current, and electron probe diameter were, respectively, 15 kV, 20 nA, and ca. 1 µm.

The XRD patterns (10.0 ≤ 2θ ≤ 70.0°) were taken from the disk surfaces of samples 4 and 5. The entire experimental diffraction patterns were employed for the Le Bail method\textsuperscript{18} to extract the integrated intensities on a computer program RIETAN-FP.\textsuperscript{19} The simulated XRD pattern of LSO polycrystal with no preferred orientation was generated using this program based on the structural parameters for La8.13Si6O26.\textsuperscript{20} Based on the Lotgering method,\textsuperscript{21} we determined the texture fraction of apatite [0 0 l] planes (Lotgering factor \textit{f}_{00l}), the detailed definition of which is given in literature.\textsuperscript{7}

With samples 4 and 5, we prepared the electrodes by coating a Pt paste on both sides of the disk surfaces, which was heated at 1023 K for 0.5 h to decompose the paste and harden the Pt residue. The thickness of sample 4 was 3.1 × 10\textsuperscript{-2} cm (≡ L), and the electrode area was 1.13 × 10\textsuperscript{-1} cm\textsuperscript{2} (≡ S). Thus, the shape factor (≡ L/S) was determined to be 2.74 × 10\textsuperscript{-1} cm\textsuperscript{-1}. The shape factor of sample 5 was 3.99 × 10\textsuperscript{-1} cm\textsuperscript{-1} (L = 9.5 × 10\textsuperscript{-2} cm, and S = 2.38 × 10\textsuperscript{-1} cm\textsuperscript{2}). The complex impedance data (4–5 MHz) were collected using an impedance analyzer (model IM3570, HIOKI E. E. Co., Nagano, Japan) during heating in air at 773–1023 K. We analyzed the equivalent circuits employing a distribution of relaxation times (DRT) analysis method on a Z-ASSIST software,\textsuperscript{22} and a nonlinear least-squares fitting method on a ZView software.\textsuperscript{23}

We cut the sample 4 into a strip and fixed onto a glass plate with epoxy resin so that the top surface of the disk was perpendicular to the slide glass plate. The sample was polished in parallel with the slide surface using a #1500 emery paper, and mirror finished by buff polishing. We carefully selected twenty-nine grains of doped LSO that were free from inclusions and cracks under the optical microscope in transmitted light. The quantitative spot analysis was made on these crystal grains using the EPMA. The concentration distribution maps were obtained for K2O, BaO, SiO2, and La2O3 in the area of 250 µm × 300 µm (250 × 300 pixels). The image data were binarized using an image processing software ImageJ\textsuperscript{24} so that the concentration distribution regions were black, and the other regions were white. The areas of these black regions were individually determined on the software. The chemical compositions of interstitial materials were semi-quantitatively determined using a scanning electron microscope (SEM; JSM-6010LA, JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDX; JED-2300, JEOL Ltd., Tokyo, Japan). The numbers of analysis points in sample 4 were eight.

The sintered specimen of sample 5 was made into thin section, and the microtexture was observed using the polarizing microscope and SEM. We determined the average chemical composition of doped LSO crystals, and that of interstitial materials using the SEM/EDX. The numbers of analysis points were five for the former material and seven for the latter.

3. Results and discussion

3.1 AGG behavior during sintering of matrix powder (sample 3)

The thin section microscopy of sample 3 showed that, during isothermal heating at 1873 K for 40 h, the AGG
predominantly occurred to form extremely large single crystals (phenocrysts) within the polycrystalline matrix, the latter of which was made up of the fine crystal grains up to 2 mm size (Fig. 1). We found, on the basis of the concentration distribution maps, no distinction between the chemical compositions of the phenocrysts and matrix (Fig. S3). The XRD pattern demonstrated that the sample 3 was composed exclusively of the apatite phase. In addition, there were no observable interstitial materials at the grain boundaries under SEM. These results strongly suggest that the AGG proceeded in the presence of a very small amount of liquid phase, which must have effectively increased the velocity of grain boundaries.

The atom ratios of sample 3 are [La:Si:Ba:O] = [8.111:5.946:1.941:26] (La + Ba = 10.052). Because the (La + Ba)-value is slightly larger than ten on basis of twenty-six O atoms, we speculate that the sample 3 was composed mainly of the BaO-doped LSO crystal with (La + Ba) = 10, together with a very small amount of coexisting liquid, the main components of which must be La2O3 and BaO. According to the phase diagram BaO–La2O3 [25] a liquid phase forms at above 1821 K in the binary system. The diagram demonstrates that the chemical composition at around 1873 K would be 70.0 mass % BaO and 30.0 mass % La2O3, corresponding to 83.2 mol % BaO and 16.8 mol % La2O3. The authors speculate that, at 1873 K, the liquid (denoted by liquid 1) with this composition forms in sample 3. Taking into consideration of both chemical compositions of liquid 1 and sample 3, we determined from calculation the plausible chemical formula of the BaO-doped LSO crystal to be (La8.12Ba1.88)Σ=10(Si15.97O10.03)Σ=6O26 (34.07 mol % La2O3, 50.12 mol % SiO2, and 15.81 mol % BaO), the mole fraction of which was determined by the lever rule to be 0.993 (Fig. S4). The mole fraction of the coexisting liquid 1 in sample 3 was therefore 0.007, which was quite small as we expected. The exact chemical compositions and the relative amounts of crystal and liquid should be investigated further, which would enhance our understanding of AGG mechanism in doped LSO crystals.

3.2 Microtextures, orientation degrees, and chemical compositions (sample 4)

The disk-shaped sample 4 was ca 17.1 mm diameter and semi-transparent under transmitted light (Fig. 2). Because the sample diameter was originally 18.0 mm, the shrinkage rate after the heat treatment was 0.05 \((= (18.0 - 17.1)/18.0)\), suggesting the occurrence of liquid phase sintering. The microtexture was observed along the direction parallel to the disk surface. The specimen was crack free, and composed mainly of the well-grown crystals of doped LSO (up to 200 μm) (Fig. 3). Each of the crystal grains was almost in the straight extinction position with respect to the disk surface under crossed polars. Because the doped LSO is of hexagonal symmetry in which the optical axis is parallel to the crystallographic c-axis, the c-axis direction of each crystal grain would be mostly perpendicular to the disk surface. Actually, the XRD pattern taken on the disk surface of sample 4 showed marked increases of 00 \((l = 2\) and 4) reflections (Fig. 4) as compared with that of the randomly oriented polycrystal (Fig. S5). The \(I_{\text{froq}}\)-value was determined to be 0.45, indicating that we successfully prepared the c-axis-aligned polycrystal of doped LSO.

The concentration distribution maps showed the presence of two types of interstitial materials between the well-grown crystals of doped LSO (Fig. 5). They would be in liquid state at 1873 K, and now glassy state at ambient temperature. One of the interstitial materials was relatively larger in amount, and rich in SiO2 component, and the other was composed of La2O3 and BaO, and free from the SiO2 component. The latter interstitial material, the locations of which are marked in Fig. 5(b), probably corresponds to liquid 1. Each of the areas with the former

Fig. 1. Optical micrographs showing the large single crystals (phenocrysts) up to 2 mm size in the polycrystalline matrix. Thin section under crossed polars. The white arrows indicate the orientations of the vibration planes of polarizer (P) and analyzer (A) of the microscope. The angle of rotation between the sample positions in (a) and (b) is 45°. The white open square in (a) depicts the EPMA mapping area for Fig. S3 (see Supplementary Information). The letters P and M in (b) mark the locations of the phenocryst and matrix, respectively. Sample 3.

Fig. 2. Optical photograph showing the semi-transparency of disk-shaped specimen, ca 310 μm thick. Transmitted light. Sample 4.
liquid, denoted by liquid 2, was large enough to individually determine the chemical compositions using EDS (Fig. S6). The relevant eight points representing their chemical compositions (Table S3) were plotted onto the La$_2$O$_3$–SiO$_2$–BaO triangular diagram (Fig. 6). The average value was 10.1(7) mol% La$_2$O$_3$, 24.4(2) mol% BaO, and 65.5(5) mol% SiO$_2$. Both components of K$_2$O and F were not detected by EDS, but we confirmed the presence of a very small amount of K$_2$O by the EPMA mapping as stated below. Because the liquid 2 contained both components of K$_2$O and BaO, it should be formed by the reaction between the K$_2$O-bearing template particles (sample 1) and BaO-bearing matrix powder (sample 2).

With doped LSO, the chemical compositions in mass % of twenty-nine crystal grains are summarized in Table S4. It should be noted that the component F was not detected. The average composition corresponds to the chemical formula of (La$_{8.43(10)}$K$_{0.03(2)}$Ba$_{1.43(5)}$□$_{0.11}$)$_{10-}$ (Si$_{5.96(8)}$□$_{0.04}$)$_{6}$O$_{26}$ (36.30 mol% La$_2$O$_3$, 0.14 mol% K$_2$O, 12.28 mol% BaO, and 51.28 mol% SiO$_2$). The individual points representing the chemical compositions

Fig. 3. Optical micrographs showing the well-grown crystals of doped LSO. Polished thin section under (a and b) closed polars in transmitted light, and (c) reflected light. The white arrows in (a and b) indicate the orientations of the vibration planes of polarizer (P) and analyzer (A) of the microscope. The angle of rotation between the sample positions in (a) and (b) is 45°. The crystal grains are almost in the straight extinction position with respect to the disk surface in (b), indicating that each of the c-axis directions of crystal grains is almost perpendicular to the surface. The white open square in (c) depicts the EPMA mapping area for Fig. 5. Sample 4.

Fig. 4. Fitting result of the observed diffraction pattern (red symbol: +) taken on the sample surface. The calculated pattern and the positions of possible Bragg reflections are, respectively, indicated by the upper solid line and the lower vertical bars. The difference curve is shown in the lower part of the diagram. Sample 4.

Fig. 5. Concentration distribution maps for (a) K$_2$O, (b) BaO, (c) SiO$_2$, and (d) La$_2$O$_3$. The white arrows in (b) mark the locations of liquid 1, which consists of La$_2$O$_3$ and BaO, and is free from SiO$_2$. Sample 4.
The compositional fluctuation around the average value was relatively significant, which was principally induced by the inhomogeneous distributions of K$_2$O component within the crystal grains. Because the amounts of coexisting liquids (liquids 1 and 2) were quite small, the average composition of doped LSO crystals was close to that of sample 4, which is located on the tie line connecting the points representing the bulk chemical compositions of samples 1 and 2 when plotted onto the La$_2$O$_3$–SiO$_2$–BaO ternary diagram (Fig. S7). The relevant point representing the average composition of sample 4 was surrounded by the three points of the above-mentioned crystals and liquids. Thus, it would be reasonable to consider that the sample 4 is made up of the three phases, the mole fraction of which was determined from the lever rule to be 0.973 for doped LSO crystals, 0.010 for liquid 1, and 0.017 for liquid 2.

When we compare the average chemical compositions between the sample 4 (Table S2) and doped LSO (Table S4), the concentrations of the main components (La$_2$O$_3$, SiO$_2$, and BaO) were almost the same, while those of the minor ones (K$_2$O and F) were quite different from each other. This would be caused, during the heat treatment at 1873 K for 50 h, by the evaporation of the minor components almost completely for F and partially for K$_2$O.

### 3.3 Compositional heterogeneity of textured ceramics (sample 4)

Within each crystal grain of doped LSO in sample 4, the concentration distributions of BaO, SiO$_2$, and La$_2$O$_3$ were found to be relatively uniform, whereas the K$_2$O concentration was heterogeneously distributed (Fig. 5). Since the ceramic powder (sample 2) is free from the K$_2$O component, it should be originated from the K$_2$O-bearing template particles (sample 1). Thus, the regions where the K$_2$O concentration is relatively high (termed “K$_2$O-distribution regions” hereafter) should correspond to those where the template particles originally existed. The individual areas of the K$_2$O-distribution regions [Fig. 5(a)] were determined from the corresponding binarized image [Fig. S8(a)], which ranged from 2089–6312 $\mu$m$^2$ with the total area being 21708 $\mu$m$^2$. During the sintering process at 1873 K for 50 h, the K$_2$O component would readily diffuse into the relatively K$_2$O-poor regions of doped LSO crystals. This would result in the K$_2$O-distribution regions to become wider as compared with the original sizes of the template particles. Actually, when viewed normal to the common c-axis-direction of the textured polycrystal, the largest area of the K$_2$O-distribution regions was 6312 $\mu$m$^2$, which was wider than the original cross-sectional area of the largest template particle of $\sim$5000 $\mu$m$^2$ (ca. 125 $\mu$m diameter and $\sim$40 $\mu$m thick).

The BaO-distribution regions, in which the BaO concentration is relatively high, correspond to those where the two types of liquids exist at the grain boundaries of doped LSO crystals [Fig. 5(b)]. The individual areas of the BaO-distribution regions were determined from the corresponding binarized image [Fig. S8(b)], which ranged from 1–84 $\mu$m$^2$ with the area in total of 658 $\mu$m$^2$. The sample 4 contained lots of voids, which were clearly recognized by the concentration distribution map of BaO, since the doped LSO crystals and coexisting liquids necessarily contained BaO component [Fig. 5(b)]. The individual areas of the voids, as determined from the corresponding binarized image [Fig. S8(c)], ranged from 1–975 $\mu$m$^2$ with the total area being 5760 $\mu$m$^2$. As a result, the whole area of 75000 $\mu$m$^2$ (= 250 $\mu$m $\times$ 300 $\mu$m) was made up of the areas of doped LSO crystals (68582 $\mu$m$^2$), two types of liquids (658 $\mu$m$^2$), and voids (5760 $\mu$m$^2$). Thus, the relative density was found from calculation to be 92.3% ($= (1 – 5760/75000) \times 100$), which agreed well with that of sample 5 (ca. 92%). As for the solid part, the area fractions were 0.990 ($= 68582/(68582 + 658)$) for the doped LSO crystals and 0.010 for the two types of liquids. These values are in accord with the mole fractions that were determined based on the chemical compositions by the lever rule; they were 0.973 for the doped LSO crystals and 0.027 for the liquids 1 and 2. For more quantitative discussion, we have to take into account the densities of these materials and to determine these fractions from much wider regions.

We have, based on the microstructure aforementioned, deduced the plausible formation process of the c-axis-aligned polycrystal of doped LSO. In the initial stage of the sintering process, the AGG of ceramic powder (sample 2) would occur, in the presence of a very small amount of liquid 1, heterogeneously on the template particles (sample 1). The BaO-doped LSO crystals would grow, incorporating the K$_2$O-bearing template particles, so as to maintain the crystal orientations between them. As the incorporating reaction proceeds, the other liquid phase (liquid 2) would be formed to accelerate the whole sintering reaction. The end result is the formation of the c-axis-aligned polycrystalline doped LSO and relatively small amounts of the two types of coexisting liquids. The resulting doped LSO is characterized by a homogeneous distribution of BaO and a heterogeneous distribution of K$_2$O within the crystal grains.
3.4 Phase and chemical compositions of randomly oriented polycrystal (sample 5)

With sample 5, all of the observable diffraction peaks in the XRD pattern (Fig. S9) were successfully assigned to LSO. In addition, the sizes of the crystal grains were relatively small and mostly ranged from ~5 to ~80 μm (Fig. S10), suggesting a relatively small amount of coexisting liquid. Actually, we found a small amount of interstitial materials (probably glassy state at ambient temperature) at the LSO grain boundaries under SEM. The chemical compositions of the crystalline and liquid phases are summarized in Tables S5 and S6. The average chemical composition of the liquid phase (62.3 mol% La2O3, 0.3 mol% BaO, and 37.5 mol% SiO2), which is characterized by the relatively low concentration in BaO, was close to that of the eutectic point at 2048 K (~62 mol% La2O3 and ~38 mol% SiO2) in the binary system La2O3–SiO2.20

The chemical composition of sample 5 was determined by the DRT analysis method, and subsequently recalculated. The initial values of time constants involved in the response. Thus, we employed the equivalent circuit consisting of the equipment (eq), bulk (b), grain boundary (gb), and electrode (e) elements that are connected in series (\(R_{\text{eq}}\)) and in parallel, respectively (\(R_{\text{b}}, \, R_{\text{gb}}, \, R_{\text{e}}\)). The resistance \(R_{\text{eq}}\) corresponds to the constant phase element \(Q\). The electrical resistance of \(R_{\text{eq}}\) was mostly induced by the conduction wires. The initial values of time constants involved in the considered system were determined by the DRT analysis method, and subsequently refined by the least-squares fitting method. The \(C_{\text{b}}\)-values (F cm\(^{-2}\)) ranged from 4.01 \times 10\(^{−11}\) at 773 K to 1.21 \times 10\(^{−10}\) at 973 K. These values agreed well with those of ceramic materials, which is generally 10\(^{−12}\)–10\(^{−11}\) F cm\(^{-2}\).27,28

The Nyquist plots in the high-frequency regions (Fig. S12) were found to be given by the convolution of the two semicircles with b and gb. As the temperature increased from 773 to 1023 K, the \(R_{\text{b}}\)-values progressively became smaller, and hence the bulk conductivity, \(\sigma_{\text{b}} = (L/S) \times (1/R_{\text{b}})\), steadily increased from 1.89 \times 10\(^{−4}\) to 2.48 \times 10\(^{−3}\) S cm\(^{-1}\) (Fig. 7). The activation energy of conduction along the grain-alignment direction (\(E_{/c}\)) was 0.783(7) eV. The total conductivity, \(\sigma_{\text{total}} = (L/S) \times (1/(R_{\text{b}} + R_{\text{gb}}))\), also steadily increased from 8.05 \times 10\(^{−5}\) to 1.31 \times 10\(^{−3}\) S cm\(^{-1}\).

With sample 5, we determined the \(\sigma_{\text{gb}}\)-values by extracting the bulk contribution from the impedance spectra based on the equivalent circuit as described above (Fig. S13). The \(C_{\text{b}}\)-values (F cm\(^{-2}\)) steadily increased from 1.04 \times 10\(^{−11}\) at 773 K to 1.54 \times 10\(^{−11}\) at 1023 K, which agreed well with those of ceramic materials as mentioned previously. The \(\sigma_{\text{gb}}\)-value steadily increased from 2.67 \times 10\(^{−5}\) to 3.42 \times 10\(^{−4}\) S cm\(^{-1}\) with increasing temperature from 773 to 1023 K (Fig. 7). The activation energy of conduction of the randomly grain-aligned polycrystal (\(E_{/c}\)) was 0.783(3) eV. When the \(\sigma_{\text{gb}}\)-values were compared between the samples 4 and 5 at the same temperatures, they were 6.7 (at 973 K)–8.2 (at 923 K) times higher for the former than for the latter (Fig. 7), with the \(E_{/c}\)- and \(E_{/\text{random}}\)-values being nearly the same. The \(\sigma_{\text{total}}\)-value steadily increased from 1.72 \times 10\(^{−5}\) (773 K) to 2.61 \times 10\(^{−4}\) S cm\(^{-1}\) (1023 K).

Since the volume fraction of non-LSO interstitial materials in each sample 4 and 5 is fairly small, it is doped LSO crystals that form the network of ionic conduction. Hence, the larger \(\sigma_{\text{b}}\)-values for the c-axis aligned material (sample 4) as compared with the randomly oriented one (sample 5) would be principally caused by the substantially higher oxide-ion conductivity along the c-axis than along the other directions in the crystal structure of K2O–BaO-doped LSO.

![Fig. 7](image-url) Comparison of oxide-ion conductivity of the c-axis-aligned polycrystal (sample 4) and randomly oriented one with the same bulk chemical composition (sample 5). Both conductivities of bulk (\(\sigma_{\text{b}}\)) and total (\(\sigma_{\text{total}}\)) of sample 4 are necessarily higher than those of sample 5 at each temperature.
4. Conclusion

We in advance prepared the two types of starting materials; they were the tabular single crystals of $K_2O$- and $F$-doped LSO as template particles, and the matrix powder consisting mainly of $BaO$-doped LSO. The template particles were mixed with the powder, and aligned by tape casting. The tapes were punched out into disk-shaped pieces, stacked in two layers, and heated at 1873 K for 50 h. The sintered material as obtained was composed of the c-axis-aligned polycrystal of $K_2O$- and $BaO$-doped LSO, and small amounts of two types of interstitial liquids. The texture fraction of apatite existing liquids was composed mainly of $BaO$ and $La_2O_3$.

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

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