Grain-oriented polycrystalline sodium titanooxaluminate formed by reactive diffusion between solid Al$_2$TiO$_5$ and liquid [25 mol% Na$_2$O and 75 mol% TiO$_2$]

Koichiro FUKUDA$^{1,³}$, Shin HASEGAWA$^1$, Eisei HASEGAWA$^1$, Daisuke URUSHIHARA$^1$ and Toru ASAKA$^1$

$^1$Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya 466–8555, Japan

We successfully prepared the c-axis-oriented polycrystalline sodium titanooxaluminate (NTAO) by the reactive diffusion between solid Al$_2$TiO$_5$ and liquid [25 mol% Na$_2$O and 75 mol% TiO$_2$]. When the Na$_2$Ti$_2$O$_7$/Al$_2$TiO$_5$ diffusion couple was isothermally heated at 1673 K for 3 h, the Na$_{0.78}$Ti$_{2.22}$Al$_{4.78}$O$_{12}$ polycrystal was readily formed in the presence of a liquid phase. The resulting polycrystalline material was characterized by X-ray diffractometry, electron microscopy, and impedance spectroscopy. We mechanically processed the annealed diffusion couple, and obtained the thin-plate electrolyte consisting mostly of the grain-aligned NTAO polycrystal. The ionic conductivity of the electrolyte along the common c-axis direction steadily increased from 1.29 × 10$^{-2}$ to 1.31 × 10$^{-2}$ S cm$^{-1}$ as the temperature increases from 923 to 1073 K, with the activation energy being 0.095 eV. The crystal structure of NTAO (space group $Pbam$) was isomorphous with that of Na$_2$Ti$_2$Al$_2$O$_7$. The Na$^+$ ions occupied ~78% of the Wyckoff position $2d$ site, the deficiency of which would contribute to the relatively high ionic conductivity along the c-axis. The present solid-liquid reactive diffusion technique could be widely applicable to the preparation of the other grain-aligned ceramics of multi-component systems.

Key-words : Sodium titanooxaluminate, Reactive diffusion, Crystalline orientation, Ionic conduction

[Received October 28, 2018; Accepted January 21, 2019]

1. Introduction

Sodium titanooxaluminate (NTAO) with one-dimensional tunnel structure has attracted much attention as potential heat-insulators as well as ionic conductors.$^{[1]-[5]}$ Fujiki et al. have propostioned the general formula of NTAO to be Na$_{x-y}$Ti$_{2+y}$Al$_{3-2y}$O$_{12}$, where $x$ represents the amount of Na$^+$ ion deficiency.$^{[3]}$ Mumme and Wadsley have determined the crystal structure of NaTi$_2$Al$_2$O$_7$ ($x = 0$), in which the Na$^+$ ion fully occupies the octahedral site within the tunnel that is made up of both [(Al/Ti)O$_6$] octahedra and [AlO$_4$] tetrahedra.$^{[6]}$ The higher occupancy of mobile Na$^+$ ions within one-dimensional tunnel, running parallel to the c-axis in the crystal structure (space group $Pbam$), would cause the higher inter-ionic potential,$^{[7]}$ which would instantly decrease the Na$^+$-ion conductivity. Thus, the authors speculate that, when the Na site was deficient to some extent, the Na$^+$ ion would relatively easily transport along the tunnel.

With sodium titanogallate (Na$_{y+3}$Ti$_{1-y}$Ga$_{4+y}$O$_{12}$, NTGO) in the ternary system Na$_2$O–Ga$_2$O$_3$–TiO$_2$, the crystal structures have been determined for Na$_{0.7}$Ti$_{0.3}$Ga$_{4.7}$O$_8$ ($y = 0.7$ and $z = 0$)$^{[8]}$ and Na$_{0.85}$Ti$_{0.51}$Ga$_{4.37}$O$_8$ ($y = 0.49$ and $z = 0.12$).$^{[9]}$ These isostructural compounds are characterized by the tunnel-like framework, which is closely related to the crystal structure of titanogallate (Ga$_4$Ti$_3$O$_{12}$).$^{[10]-[13]}$ The amount of Na$^+$-ion deficiency is 30% for the former NTGO compound, and 15% for the latter. Chandrashekar et al. have grown the single crystal of Na$_{0.7}$Ti$_{0.3}$Ga$_{4.7}$O$_8$ to demonstrate the anisotropy of conductivity.$^{[8]}$ Actually, the Na$^+$ ions easily transported along the tunnels in parallel with the crystallographic b-axis (space group $C2/m$). The conductivity ($\sigma$) at 573 K was 1 × 10$^{-2}$ S cm$^{-1}$, which was ca. 2000 times higher than that perpendicular to this direction.

To readily prepare the crystal-oriented ceramics, Fukuda et al. have recently developed a novel technique of reactive diffusion.$^{[14]-[18]}$ This technique has been originally applied to the fabrication of polycrystalline lanthanum silicate oxyapatite (LSO; La$_{0.33}$Si$_2$O$_6$), in which the oxidation relatively rapidly conducts along the c-axis in the crystal structure (space group $P6_3/m$). The highly c-axis-oriented LSO polycrystal has been instantly formed, as the result of heating at 1773–1873 K for 5–100 h in air, at the interfacial contact boundary of La$_2$Si$_3$O$_7$/La$_2$Si$_2$O$_7$ diffusion couple.$^{[14]}$ Because this reaction necessarily occurs and proceeds between the solid-state diffusion couples, it can be classified as solid-solid reactive diffusion. The c-axis-oriented polycrystalline LSO has also been prepared

Corresponding author: K. Fukuda; E-mail: fukuda.koichiro@nitech.ac.jp
by the solid-gas reactive diffusion, in which the solid La2SiO5 reacts with gases [SiO + 1/2O2] to form the product.10) The SiO gas can be continuously generated by the heat treatment of the powder mixture of Si and SiO2 at 1873 K under the oxygen partial pressure of carbon-carbon monoxide buffer.

The reactive diffusion for LSO occurs in the binary system La2O3–SiO2, which includes the three relevant compounds (La2SiO5, LSO, and La2Si2O5). On the other hand, in the ternary system Na2O–Ga2O3–TiO2, Hasegawa et al. have applied the reactive diffusion technique to fabricate the b-axis-oriented polycrystalline NTAO.9) They have prepared the sandwich-type Ga2TiO5/NaGaO2/Ga2TiO5 diffusion couple, and then heated it at 1323 K for 24 h in air to obtain the grain-aligned polycrystalline Na0.83Ti0.51Ga4.73O8 with a small amount of Ga2O3-doped Na2Ti4O9 (G-NTO) as matrix that was in a liquid state at high temperatures and crystallized on cooling. The characteristic feature of this reaction is that, when the chemical compositions are adopted, the two types of reactive diffusion occur between two solids and the other proceeds between a solid and gases. In the present study, we have for the first time applied the reactive diffusion technique to fabricate the crystal-oriented ceramics of multi-component systems.9)

As outlined above, the two types of reactive diffusion techniques have been established so far, one of which occurs between two solids and the other proceeds between a solid and gases. In the present study, we have for the first time applied the solid–liquid reactive diffusion technique for the fabrication of crystal-oriented ceramics. We have, in the ternary system Na2O–Al2O3–TiO2, assembled the diffusion couple of solid Al2TiO5 and liquid [25 mol % Na2O and 75 mol % TiO2] to successfully prepare the c-axis-oriented polycrystalline NTAO. We clarified the crystal structure of the constituent NTAO as well as the Na+ ion conductivity along the common c-axis of the polycrystal at 923–1073 K.

2. Experimental procedures

2.1 Materials

Two types of powder mixtures in molar ratios of [Na2CO3:TiO2] = [1:3], and [Al2O3:TiO2] = [1:1] were prepared from reagent-grade chemicals of Na2CO3 (99.5%, Kishida Chemical Co. Ltd., Osaka, Japan), TiO2 (99.5%, Kishida Chemical Co. Ltd.), and Al2O3 (99.0%, Kishida Chemical Co. Ltd.). We heated the former mixture at 1223 K for 6 h, and the latter at 1773 K for 24 h, and obtained the slightly sintered polycrystalline materials of Na2Ti3O7 and Al2TiO5, each of which was subsequently ground into fine powder specimen. We uniaxially pressed each of them, and prepared the Na2Ti3O7 pellets (0.881 g each) with the size of φ13 mm × 3.6 mm, and the Al2TiO5 pellets (1.594 g each) with the size of φ18 mm × 2.3 mm. The Na2Ti3O7/Al2TiO5 diffusion couples, consisting of 25.0 mol % Na2Ti3O7 and 75.0 mol % Al2TiO5, were assembled by joining the two types of pellets with top Na2Ti3O7 and bottom Al2TiO5. We heated these couples at 1673 K for 3 h, and then quenched them to ambient temperature by cutting furnace power. During heating at that temperature, Na2Ti3O7 (m.p. = 1401 K) completely melted, and reacted with solid Al2TiO5 (m.p. = 2133 K) to form NTAO and TiO2-rich liquid, the latter of which was crystallized to NaAlTi3O8 on quenching.

We also prepared the randomly grain-oriented polycrystalline Na0.78[Ti2.22Al4.78]O12 (α = 0.22) from the stoichiometric amounts of the chemicals of Na2CO3, TiO2, and Al2O3 ([Na2CO3:TiO2:Al2O3] = [0.39:2.22:2.39] in molar ratios). The powder mixture was pressed into pellets, heated at 1273 K for 1 h, and followed by quenching in air. The slightly sintered material was ground to a fine powder, pressed into pellets, and heated at 1673 K for 48 h to eventually obtain the sintered pellets (φ13 mm × 1.811 mm) with the relative density (measured density over theoretical density) of ca. 97%.

2.2 Scanning electron microscopy and optical microscopy

We embedded one of the annealed couples in resin, and cut it using a diamond saw to expose section, the surface of which was perpendicular to the former NTAO/Al2TiO5 boundary (parallel to the grain-alignment direction of NTAO). The section surface was polished with 1-μm diamond paste, and the microtexture on the surface was observed using a scanning electron microscope (SEM: JSM-6010LA, JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray analyzer (EDX; JED-2300, JEOL Ltd., Tokyo, Japan). We subsequently made the polished section into thin section, and its microtexture was observed using a polarizing microscope in transmitted light.

2.3 Orientation degree and Na+ ion conductivity

We equally ground both sides of the annealed couple with 800-grid SiC paper, finally polished with 1-μm diamond paste, and obtained the thin plate of electrolyte (ca. 330 μm thickness), which corresponds to the innermost part of the annealed couple. The electrolyte plate was mostly composed of the c-axis-aligned polycrystalline NTAO with small amounts of NaAlTi3O8 and unreacted Al2TiO5.

We collected the X-ray profile intensity data on the flat surface of the electrolyte plate using an X-ray powder diffractometer (X’Pert PRO Alpha-1, PANalytical B. V., Almelo, the Netherlands) in the range of 10.0° ≤ 2θ (Cu Kα1) ≤ 90.0° (2394 total data points). The integrated reflection intensities of the constituent three phases (NTAO, NaAlTi3O8, and Al2TiO5) were extracted from the whole X-ray diffraction (XRD) pattern using the Le Bail method10 on a computer program Rietan-FP.20 The simulated reflection intensities of the NTAO (α = 0.22)
with random grain orientation were determined from calculation using the same program. Based on the observed and calculated reflection intensities, we determined the Lotgering factor \( f_{\text{lot}} \) value, which represents the texture fraction of [001] planes.

The Pt paste was coated on both sides of the electrolyte plate, and the Pt residue was hardened by the heat treatment at 1023 K for 0.5 h. We collected the complex impedance data (4–5 MHz) during heating from 923 to 1073 K using an impedance analyzer (model IM3570, HIOKI E. E. Co., Nagano, Japan). We employed a non-linear least square fitting method using a ZView software to analyze the equivalent circuits, and determined the bulk conductivity.

2.4 Single-crystal X-ray diffraction and bond-valence-sum mapping

After the conductivity measurement, a single crystal (45 \( \mu \text{m} \times 30 \mu \text{m} \times 10 \mu \text{m} \)) was picked up from the electrolyte plate, and mounted on the end of a glass capillary. The XRD intensities were measured on a diffractometer (Bruker D8 VENTURE) using Mo K\( \alpha \) radiation (50 kV and 1 mA). We determined the observed structure factors, based on the refined unit-cell dimensions, on a program package APEX3 Suite. The structural parameters as well as the atomic displacement parameters were refined on a computer program JANA2006. We used a computer program VESTA for the drawing of the ball-and-stick model. The structural data was standardized, based on the rules formulated by Parthé and Gelato, on a computer program STRUCTURE TIDY, the subroutine of which was implemented in the program VESTA. The crystal information, and the parameters for data collection and refinement are summarized in Table 1.

The spatial distributions of bond valence (BV) \(^{20,29}\) values have successfully demonstrated the interaction on the topology of ion-conduction pathways. \(^{30,31}\) We used a computer program PyAbstantia \(^{22}\) for this calculation, in which the modified ‘soft-BV’ parameters \( r_0 \) and \( B \) are adopted for the expanded evaluation range of the bonding interaction. This program outputs the deviation of BV sum (BVS) from the ideal valence of the target ion:

\[
|\Delta V| = |V_{\text{target}} - V_{\text{ideal}}|
\]

The distributions of BV-values for Na\(^+\) was found from calculation with the resolution of 0.01 nm/voxel. The \( r_0 \)- and \( B \)-values are, respectively, 1.56225 and 0.482 for Na-O bond. \(^{30}\) We excluded the penalty term of asymmetric coordinate from the calculation. The three-dimensional conduction paths of Na\(^+\) were depicted as isosurface curves of |\( \Delta V \)|, and visualized using the computer program VESTA. As the isosurface level is lower, it tends to conduct the Na\(^+\) ion easier.

3. Results and discussion

3.1 Microtextures and chemical compositions

The annealed couples as obtained were disc shaped with the size of \( \phi \) ca. 18 mm \( \times \) ca. 2.7 mm. The backscattered electron composition (BEC) images on the section surface (Fig. 1) as well as the thin-section micrographs (Fig. 2) revealed that each of the annealed couples consisted of a three-layered structure. The layer thicknesses in the selected region of Fig. 2 were ca. 550 \( \mu \text{m} \) for the upper part, ca. 2050 \( \mu \text{m} \) for the middle part, and ca. 100 \( \mu \text{m} \) for the lower part.

The middle part as shown in Fig. 1(d) was mostly made up of the columnar crystals of NTAO with small amounts of coexisting materials, which were NaAlTi\(_3\)O\(_8\) and unreacted Al\(_2\)TiO\(_5\) as it turned out by XRD and EDX. The elongation directions of the NTAO crystals were almost perpendicular to the former Na\(_2\)Ti\(_3\)O\(_7\) system being orthorhombic. Most of the columnar crystals of NTAO with the significantly weaker reflections of NaAlTi\(_3\)O\(_8\) and Al\(_2\)TiO\(_5\) boundary. When observed under the polarizing microscope, each NTAO crystal showed straight extinction curves of \( l = 1 \) and 2) reflections in comparison with those of the randomly grain-oriented NTAO (Fig. S1). We determined from calculation the \( f_{\text{lot}} \) value to be 0.75. All of the observed reflections were successfully assigned to those of NTAO with the significantly weaker reflections of NaAlTi\(_3\)O\(_8\) and Al\(_2\)TiO\(_5\).

In general, the brightness on the flat surface principally depends on the material’s density for BEC images.
Because of the higher density \(D/\text{Mg m}^{-3}\) for NaAlTi\(_3\)O\(_8\) \((D = 3.82)\) than for NTAO \((D = 3.60)\) and Al\(_2\)TiO\(_5\) \((D = 3.68)\), the former material was brighter than the others, and hence its distribution texture was clearly recognized on the micrograph. In the middle part of the annealed couple, the NaAlTi\(_3\)O\(_8\) crystals were found as the interstitial material between the columnar NTAO crystals [Fig. 1(d)]. We examined the NaAlTi\(_3\)O\(_8\) matrix using EDX to confirm the \([\text{Na}:\text{Al}:\text{Ti}]\) atom ratios to be nearly \([1:1:3]\), which is in agreement with the chemical formula of NaAlTi\(_3\)O\(_8\) (Fig. S2). In light of the microtexture of NaAlTi\(_3\)O\(_8\) matrix, it must be in the liquid state at 1673 K, and crystallized on cooling. Accordingly, the solid Al\(_2\)TiO\(_5\) would react with the liquid [25 mol \% Na\(_2\)O and 75 mol \% TiO\(_2\)] at 1673 K to form the columnar NTAO crystals and the interstitial NaAlTi\(_3\)O\(_8\) melt.

We carefully examined the region of Fig. 1(d) to find the unreacted Al\(_2\)TiO\(_5\) crystals, each of which were granular in shape with the size less than 50 \(\mu\text{m}\) (Fig. S3). We determined the chemical composition by EDX to confirm the \([\text{Al}:\text{Ti}]\) atom ratios to be nearly \([2:1]\), which is in accord with the corresponding chemical formula.

The upper part of the annealed couple [Fig. 1(c)], probably corresponding to the former Na\(_2\)Ti\(_3\)O\(_7\) region, was mainly composed of NaAlTi\(_3\)O\(_8\) with a small amount of NTAO. The thin polycrystal layer of NaAlTi\(_3\)O\(_8\), located at the bottom of the annealed diffusion couple, would be the crystallized melt, which would be, during heating at 1673 K for 3 h, steeped out through the interstitial opening of the NTAO polycrystal.

### 3.2 Crystal structure refinement

The single crystal of NTAO showed the intensity distributions that are consistent with the Laue symmetry \(mmm\). Thus, we have constructed the initial structural model in reference to the crystal structure of NaTi\(_2\)Al\(_5\)O\(_{12}\) (space group \(Pbam\) and \(Z = 2\)) reported by Mumme and Wadsley.\(^6\) There are one Na site (Wyckoff position 2\(d\)), four Ti/Al sites (Ti/Al\(_1\) of 4\(h\), Ti/Al\(_2\) of 2\(a\), Ti/Al\(_3\) of 4\(g\), and Ti/Al\(_4\) of 4\(h\)), and six O sites (O\(_1\), O\(_4\) and O\(_5\) of 4\(h\), and O\(_2\), O\(_3\) and O\(_6\) of 4\(g\)) in the asymmetric unit. The occupancies (\(g\)) of Ti and Al in each Ti/Al site was determined by imposing the linear constraints of \(g(\text{Ti}) + g(\text{Al}) = 1\). The Ti/Al\(_4\) site was found to be exclusively occupied by Al, hence this site was relabeled as Al. The \(g\)-value of Na site, together with those of Ti/Al\(_1\)–Ti/Al\(_3\) sites, were refined under the charge balance constraints. After the refinement based on the anisotropic atomic displacement parameters (ADPs) for all sites, the resulting...
difference Fourier maps showed negligible residual electron density ($\Delta \rho / \text{nm}^3$) distributions of $\Delta \rho_{\text{max}} = 0.33 \times 10^{-3}$ and $\Delta \rho_{\text{min}} = -0.37 \times 10^{-3}$. We eventually obtained the satisfactory reliability ($R$) indices of $R = 0.0181$ and $wR = 0.0251$. The final structural parameters and ADPs are given in Table 2. The Na site was found to be partially occupied with $g(\text{Na}) = 0.780(8)$. Thus, the chemical formula was determined to be $\text{Na}_{0.780(8)}\text{Ti}_{2.22(2)}\text{Al}_{4.78(2)}\text{O}_{12}$ ($x \approx 0.22$). The ball-and-stand structural model is given in Fig. 4(a).

Since the site occupancy of $\text{Na}^+$ was less than unity, the composition was charge balanced by replacing a fraction of $\text{Al}^{3+}$ ions at the octahedral sites ($\text{Ti}^{4+}/\text{Al}^{3+}$) by $\text{Ti}^{4+}$ ions according to the formula $[\text{Na}_{1-x}]^Q[\text{Ti}_{1-2x/3}\text{Al}_{1-3x/3}]^{V_L}\text{Al}^{3+}\text{O}_{12}$ ($x \approx 0.22$). The $\text{Al}^{3+}$ ions at the tetrahedral site were free from the replacement. The atom arrangements were principally in accord with those of $\text{NaTi}_2\text{Al}_5\text{O}_{12}$ ($x = 0$).6

Based on the selected bond lengths for NTAO (Table S1), we determined from calculation the charge distribution.34,35 The ratio of formal oxidation number ($q$) to computed charge ($Q$) for each cation site ($= q/Q$) quantitatively evaluates the correctness of the charge determination. These ratios ranged from 0.967 for O1 site to 1.102 for O5 site (Table S2). All these ratios are close to unity, hence we concluded that the final structural model was reasonably satisfactory.

### 3.3 Ionic conduction pathway and conductivity

The differences in BVS from the ideal values as isosurfaces were generated based on the structural models of NTAO and $\text{NaAlTi}_3\text{O}_8$ (Fig. S4).36 With NTAO, the three-dimensional BVS map showed the one-dimensional pathways of $\text{Na}^+$ along the [001] direction [Fig. 4(b)]. The pathways were constructed for the isosurface levels with $|\Delta V| \geq 0.04$. The thermal-motion probability ellipsoid of the Na site, which was described by the three principal values of mean squared displacements (MSDs), showed an unusually elongated outer shape along the ionic pathway demonstrated by BVS mapping. Actually, the ratio of largest/smallest principal MSD values was ca. 15.06, which strongly suggests the high ionic conductivity along the $c$-axis. We also visualized the three-dimensional BVS map for $\text{NaAlTi}_3\text{O}_8$ (Fig. S5). Even though the $|\Delta V|$ values were relatively large up to 1.37, the isosurfaces were necessarily displayed as the disjoint curves, which strongly suggests the impossibility of $\text{Na}^+$ conduction. Accordingly, the $\sigma$-value of the electrolyte plate would entirely correspond to the $\text{Na}^+$-ion conductivity of the polycrystalline NTAO along the $c$-axis.

We have adopted the equivalent circuit, in which the three types of elements corresponding to bulk (b), grain boundary (gb), and electrode (e) are connected in series as $R_b(R_{gb}Q_b)(R_eQ_e)$, where $R$ is a resistance parallel to a constant phase element $Q$. The $R_b$ values were extracted from the high frequency intercepts of the gb semicircles. The capacitance ($C$) values were estimated according to

$$C = Q_b(\omega_{\text{max}})^{n-1}$$

where $Q_b$ is numerically equal to the admittance (1/$|Z|$) at $\omega = 1$ rad/s, $n$ parameter describes the width of dielectric relaxation-time distribution and the imaginary part of the impedance reaches a maximum at the frequency of $\omega_{\text{max}}$.37 Each of the Nyquist plots at 923–1073 K (Fig. S6) consisted of a semicircle, corresponding to the contribu-

### Table 2. Structural parameters and atomic displacement parameters ($\times 10^{-2}$ nm$^2$) for $\text{Na}_{0.78}\text{Ti}_{2.22}\text{Al}_{4.78}\text{O}_{12}$ (NTAO)

| Site  | Wyckoff position | $g$   | $x$   | $y$   | $z$   |
|-------|------------------|------|------|------|------|
| Na    | 2$d$             | 0.780(8) | 0 | 1/2 | 1/2 |
| T1/A1 | 4$h$             | 0.884(2)/0.116 | 0.22926(2) | 0.144570(12) | 1/2 |
| T1/A2 | 2$a$             | 0.178(5)/0.822 | 0 | 0 | 0 |
| T1/A3 | 4$g$             | 0.137(3)/0.863 | 0.00948(3) | 0.300200(19) | 0 |
| Al    | 4$h$             | 1 | 30.829(4) | 0.35444(2) | 1/2 |
| O1    | 4$h$             | 1 | 0.10563(8) | 0.05178(5) | 1/2 |
| O2    | 4$g$             | 1 | 0.36214(8) | 0.10943(5) | 0 |
| O3    | 4$g$             | 1 | 0.13356(8) | 0.20429(5) | 0 |
| O4    | 4$h$             | 1 | 0.38740(8) | 0.24857(5) | 1/2 |
| O5    | 4$h$             | 1 | 0.11339(8) | 0.35013(5) | 1/2 |
| O6    | 4$g$             | 1 | 0.36260(8) | 0.40696(5) | 0 |

Space group: $Pbam$. Unit-cell dimensions: $a = 0.90676(4)$ nm, $b = 1.55240(8)$ nm, $c = 0.29170(1)$ nm, and $V = 0.41061(3)$ nm$^3$.}
tion of \( R_{gb} \) element with \( C_{gb}/\text{F cm}^{-1} = 2.9 \times 10^{-8} \) (923 K) = 1.4 \times 10^{-8} (1073 K). These values agreed well with those of ceramic materials, which generally range from \( 10^{-8} \) to \( 10^{-11} \text{F cm}^{-1}. \) The fitting results are displayed in blue solid-lines with the extrapolation to the horizontal axis. These intersection points correspond to the \( R_{gb} \)-values, which progressively became larger with decreasing temperature to 923 K.

The \( \sigma \)-value steadily increased from \( 1.29 \times 10^{-2} \) to \( 1.31 \times 10^{-2} \text{S cm}^{-1} \) with increasing temperature from 923 to 1073 K (Fig. 5). We found, over the temperature examined, the linearity of the Arrhenius plot of \( \sigma \), and hence determined the activation energy of conduction (\( E_a \)) to be 0.095(4) eV. This value was comparable to those reported for sodium \( \beta^\prime \)-alumina (\( E_a = 0.0939 \)) and 0.39 eV with 600 K < \( T \) < 1093 K (41).

We extracted the electrolyte plate from the inner most part of the annealed couple, the microtexture of which was very similar to that in Fig. 1(d). The BEC image shows two distinct areas consisting of the brighter [\( \text{NaAlTi}_3\text{O}_8 \)] and darker region of [\( \text{NTAO and Al}_2\text{TiO}_5 \)]. The ratio between the overall cross-sectional area (\( A_O \)) and the partial cross-sectional area for the NTAO and Al\(_2\)TiO\(_5\) crystals (\( A_C \)) was 0.893 (\( A_C/A_O \)). Accordingly, when we prepared the dense electrolyte material consisting exclusively of the \( c \)-axis-oriented NTAO, the conductivity at each temperature would be more than 1.12 (\( A_C/A_O \)) times higher than that of the present electrolyte; the \( \sigma \)-value at 923 K, for example, would be more than 1.44 \( \times 10^{-2} \) (\( = 1.29 \times 10^{-2} \times 1.12 \)) S cm\(^{-1} \) for the supposed electrolyte.

With the randomly grain-oriented polycrystalline Na\(_{0.78}\)Ti\(_{2.22}\)Al\(_{4.78}\)O\(_{12} \) (\( \chi = 0.22 \)), the \( \sigma \)-value steadily increased from 4.66 \( \times 10^{-3} \) to 5.15 \( \times 10^{-3} \text{S cm}^{-1} \) as the temperature increases from 923 to 1073 K (Fig. 5). The \( E_a \)-value was 0.142(1) eV, which was ca. 1.5 times larger than that of the \( c \)-axis-oriented polycrystalline NTAO. The \( \sigma \)-values of NTAO were, when compared at the same temperature, found to be more than 2.5 times higher for the grain-aligned polycrystal than for the randomly grain-oriented one.

At 923 K \( \leq T \leq 1073 \) K, the \( \sigma \)-values of the \( c \)-axis-oriented polycrystalline NTAO were found to be more than 1.8 times higher than those of the \( b \)-axis-oriented NTGO (Fig. 5). In addition, the \( E_a \)-value along the tunnel direction of NTAO was about a quarter of that of NTGO (\( E_a = 0.39 \) eV with 823 K < \( T \leq 1073 \) K (9)). Accordingly,
on the basis of the $\sigma$- and $E_c$-values, it can be concluded that the crystal-oriented polycrystal of NTAO is, as the Na$^+$-ion conductor, superior to that of NTGO.

### 3.4 Characteristics of the reactive diffusion between solid and liquid

The reaction products in annealed diffusion couples were found to be of the polycrystalline NTAO and NaAlTi$_3$O$_8$ melt, the latter of which was crystallized on cooling. We plotted the chemical compositions of these compounds in the Na$_2$O–TiO$_2$–Al$_2$O$_3$ ternary diagram to show that the tie line between the relevant points and the connecting line between Al$_2$TiO$_3$ and Na$_2$Ti$_3$O$_7$ cross at point $P_1$ in the diagram, which corresponds to ca. 10.0 mol% Na$_2$O, ca. 60.0 mol% TiO$_2$, and ca. 30.0 mol% Al$_2$O$_3$ (Fig. 6). Because the bulk chemical composition of the present diffusion couple was close to that of the intersection $P_1$, the whole diffusion couple was almost converted to the NTAO crystal and NaAlTi$_3$O$_8$ melt after the heat treatment. The conversion reaction from the reactants of [Al$_2$TiO$_3$] and [Na$_2$Ti$_3$O$_7$] to the products of [NTAO] and [NaAlTi$_3$O$_8$] is described by

$$A[Al_2TiO_3] + B[Na_2Ti_3O_7] \rightarrow C[NTAO] + D[NaAlTi_3O_8]$$

where $A$, $B$, $C$, and $D$ are the reaction coefficients. Each of the ratios $[A:B]$ and $[C:D]$ was readily determined from the chemical composition $P_1$; the former ratio was [0.750:0.250] and the latter was [0.450:0.550].

In the temperature-rising process of the Na$_2$Ti$_3$O$_7$/Al$_2$TiO$_3$ diffusion couple, the Na$_2$Ti$_3$O$_7$ pellet would instantly melt at around 1401 K. This melt would readily react with the Al$_2$TiO$_3$ pellet at the interphase boundary to form the NTAO crystallites and NaAlTi$_3$O$_8$ melt. During further heating up to 1673 K, the columnar-shaped NTAO crystals would successively grow downwards (towards the unreacted Al$_2$TiO$_3$ region) in the presence of melt, until the whole diffusion couple is eventually converted to the mixture of NTAO crystal and NaAlTi$_3$O$_8$ melt. During the isothermal annealing process, the Na$_2$O component of the Na$_2$Ti$_3$O$_7$ melt would one-dimensionally diffuse downwards the unreacted Al$_2$TiO$_3$ region. On the other hand, the Al$_2$O$_3$ component of Al$_2$TiO$_3$ region would flow upwards the former Na$_2$Ti$_3$O$_7$ region. These two opposite directional fluxes with different chemical components could be closely related to the driving force for the formation of column-shaped NTAO crystals as well as the grain alignment in the former Al$_2$TiO$_3$ region. On cooling, the crystallites of NaAlTi$_3$O$_8$ would be formed from the interstitial liquid. The end result is the mixture of columnar NTAO phenoecrys and NaAlTi$_3$O$_8$ as matrix.

In our previous studies, we succeeded in preparing the highly $c$-axis-aligned polycrystalline LSO by the reactive diffusion between the two solids [La$_2$SiO$_5$(s) and La$_2$Si$_2$O$_7$(s)]$^{14-17}$ and between the solid and gases [La$_2$SiO$_5$(s), SiO(g), and O$_2$(g)].$^{18}$ The present study has reported, for the first time, the successful preparation of the grain-aligned ceramics material using the reactive diffusion between solid and liquid. The relevant reaction, which occurs in the ternary system Na$_2$O–TiO$_2$–Al$_2$O$_3$, is characterized by the two intersecting tie-lines, one of which connects the reactants on the diagram, and the other connects the products (Fig. 6). The authors think that one of the most significant implications of this research is that we have successfully established the solid–liquid reactive diffusion technique, in addition to the already-known techniques of solid–solid and solid–gas reactive diffusion. The present solid–liquid reactive diffusion technique could be widely applicable to the other grain-aligned materials of multi-component systems.

### 4. Conclusions

We were successful in preparing the $c$-axis-oriented polycrystalline Na$_{0.78}$Ti$_{2.22}$Al$_{4.78}$O$_{12}$ (NTAO), which was embedded in NaAlTi$_3$O$_8$ matrix, by the reactive diffusion between solid Al$_2$TiO$_3$ and liquid [25 mol% Na$_2$O and 75 mol% TiO$_2$]. The crystal structure of NTAO was isomorphous with that of NaTi$_2$Al$_5$O$_{12}$. The occupancy was ~78% for the Na$^+$ site in the crystal structure of NTAO, hence the composition was charge balanced by replacing a fraction of Al$^{3+}$ ions at the octahedral sites by Ti$^{4+}$ ions. The deficiency of Na site would contribute to the relatively high ionic conductivity along the $c$-axis. The conductivity of the electrolyte consisting mostly of the $c$-axis-oriented NTAO steadily increased from 1.29 × $10^{-2}$ to 1.31 × $10^{-2}$ S cm$^{-1}$ with increasing temperature from 923 to 1073 K, with the activation energy being 0.095 eV. The conductivity values were, when compared at the same temperatures, found to be more than 2.5 times higher for the grain-aligned polycrystal than for the randomly grain-oriented one. The present solid–liquid reactive diffusion technique could be widely applicable to the preparation of the other grain-aligned ceramics of multi-component systems.

**Acknowledgment** This research was supported by JSPS KAKENHI Grant Number JP16H02396.
Appendix A. Supporting information Supplementary data associated with this article can be found in the on line version.

References
1) S. Yoshikado, T. Ohachi, I. Taniguch, M. Watanabe, Y. Fujiki and Y. Onoda, Solid State Ionics, 35, 377–385 (1989).
2) M. Watanabe, Y. Fujiki, S. Yoshikado and T. Ohachi, Solid State Ionics, 35, 369–375 (1989).
3) Y. Fujiki, M. Watanabe, Y. Onoda, S. Yoshikado and T. Ohachi, J. Ceram. Soc. Jpn., 98, 1169–1171 (1990).
4) Y. Michiu, T. Mistuhashi and Y. Fujiki, Gypsum Lime, 232, 152–158 (1991).
5) Y. Fujiki, T. Nishio and M. Watanabe, J. Ceram. Soc. Jpn., 100, 54–58 (1992).
6) W. G. Mumme and A. D. Wadsley, Acta Crystallogr., 23, 754–758 (1967).
7) H. U. Beyeler, L. Pietronero, S. Strässler and H. J. Wiesmann, Phys. Rev. Lett., 38, 1532–1535 (1977).
8) G. V. Chandrashekar, A. Bednowitz and S. J. La Placa, Fast Ion Transport in Solids, 447–450 (1979).
9) R. Hasegawa, M. Okabe, T. Asaka, N. Ishizawa and K. Fukuda, J. Solid State Chem., 229, 252–259 (2015).
10) N. Empie and D. Edwards, Solid State Ionics, 177, 77–87 (2006).
11) D. D. Edwards, N. H. Empie, N. Meethong and J. W. Amoroso, Solid State Ionics, 177, 1897–1900 (2006).
12) J. W. Amoroso and D. D. Edwards, Solid State Ionics, 179, 878–880 (2008).
13) L. A. Bursill, Acta Crystallogr. B, 35, 530–538 (1979).
14) K. Fukuda, T. Asaka, R. Hamaguchi, T. Suzuki, H. Oka, A. Berghout, E. Béchade, O. Masson, I. Julien, E. Champion and P. Thomas, Chem. Mater., 23, 5474–5483 (2011).
15) K. Fukuda, T. Asaka, S. Hara, M. Oyabu, A. Berghout, E. Béchade, O. Masson, I. Julien and P. Thomas, Chem. Mater., 25, 2154–2162 (2013).
16) K. Fukuda, T. Asaka, S. Hara, A. Berghout, E. Béchade, O. Masson, J. Jouin and P. Thomas, Cryst. Growth Des., 15, 3435–3441 (2015).
17) K. Fukuda, M. Okabe and T. Asaka, J. Am. Ceram. Soc., 99, 2816–2822 (2016).
18) K. Fukuda, R. Hasegawa, T. Kitagawa, H. Nakamori, T. Asaka, A. Berghout, E. Béchade, O. Masson, J. Jouin and P. Thomas, J. Solid State Chem., 235, 1–6 (2016).
19) A. Le Bail, H. Duroy and J. L. Fourquet, Mater. Res. Bull., 23, 447–452 (1988).
20) F. Izumi and K. Momma, Solid State Phenom., 130, 15–20 (2007).
21) F. K. Lotgering, J. Inorg. Nucl. Chem., 9, 113–123 (1959).
22) D. Johnson, ZView Program, Version 2.9b; Scribner Associates, Inc. Southern Pines, NC (1990).
23) APEX3 Suite, version 2015.07; Bruker Analytical X-ray System Inc.: Madison, WI (2015).
24) V. Petricek, M. Dusek and L. Palatinus, JANA2006: The Crystallographic Computing System; Institute of Physics: Praha, Czech Republic (2006).
25) K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272–1276 (2011).
26) E. Parthé and L. M. Gelato, Acta Crystallogr. A, 40, 169–183 (1984).
27) L. M. Gelato and E. Parthé, J. Appl. Crystallogr., 20, 139–143 (1987).
28) I. D. Brown and D. Altermatt, Acta Crystallogr. B, 41, 244–247 (1985).
29) N. E. Brese and M. O’Keeffe, Acta Crystallogr. B, 47, 192–197 (1991).
30) S. Adams, Appl. Energ., 90, 323–328 (2012).
31) S. Adams and R. P. Rao, Struct. Bond., 158, 129–159 (2014).
32) P. Barpanda, G. Oyama, S. Nishimura, S.-C. Chung and A. Yamada, Nat. Commun., 5, 4358 (2014).
33) S. Adams and R. P. Rao, Phys. Status Solidi A, 208, 1746–1753 (2011).
34) R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller and K. Bernet, J. Less-Common Met., 156, 105–122 (1989).
35) M. Nespolo, G. Ferraris and H. Ohashi, Acta Crystallogr. B, 55, 902–916 (1999).
36) A. V. Knyazev, M. Maćzka, I. V. Ladenkov, E. N. Bulanov and M. Ptak, J. Solid State Chem., 196, 110–118 (2012).
37) C. H. Hsu and F. Mansfeld, Corrosion, 57, 747–748 (2001).
38) J. T. S. Irvine, D. C. Sinclair and A. R. West, Adv. Mater., 2, 132–138 (1990).
39) J. L. Briant and G. C. Farrington, J. Solid State Chem., 33, 385–390 (1980).
40) P. K. Davies, F. Garzon, T. Feist and C. Katzman, Solid State Ionics, 18–19, 1120–1128 (1986).
41) M. S. Whittingham and R. A. Huggins, J. Chem. Phys., 54, 414–416 (1971).