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Structure and ionic conductivity of well-aligned polycrystalline sodium titanogallate grown by reactive diffusion

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ABSTRACT

We prepared the *b*-axis-oriented polycrystalline $Na_{0.85}Ti_{0.51}Ga_{4.37}O_8$ (NTGO) embedded in Ga_2O_3-doped $Na_2Ti_4O_9$ matrix using the reactive diffusion technique. When the sandwich-type $Ga_2TiO_5/NaGaO_2/Ga_2TiO_5$ diffusion couple was heated at 1323 K for 24 h, the NTGO 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 NTGO polycrystal. The ionic conductivity (σ) of the electrolyte along the common *b*-axis direction steadily increased from 1.3×10^{-4} to 7.3×10^{-3} S/cm as the temperature increased from 573 to 1073 K. There was a slope change at ca. 792 K for the Arrhenius plot of σ; the activation energies were 0.39 eV above this temperature and 0.57 eV below it. The NTGO showed the crystal structure (space group *C*2/*m*) with substantial positional disordering of one of the two Ga sites. The Na^+ ions occupied ca. 43% of the Wyckoff position 4*i* site, the deficiency of which would contribute to the relatively high ionic conductivity along the *b*-axis. The reactive diffusion could be widely applicable as the novel technique to the preparation of grain-aligned ceramics of multi-component systems.

1. Introduction

Sodium titanogallates with one-dimensional tunnel structures are interesting materials for their potential application as solid electrolytes because of the availability for fast ion transport within the tunnels [1–9]. The sodium-ion conductor with the general formula $Na_{1-X+3Y}Ga_{5-X-Y}Ti_XO_8$, which is equivalent to $Na_{x+3y}Ti_{1-x}Ga_{4+x-y}O_8$ (NTGO), has been for the first time reported by Chandrashekar et al. [1] They have grown the single crystals of $Na_{0.7}Ti_{0.3}Ga_{4.7}O_8$ ($x=0.7$ and $y=0$) to demonstrate the anisotropy of ionic conduction. The framework of the crystal structure (space group *C*2/*m*, $a=1.2363$ nm, $b=0.3002$ nm, $c=0.9362$ nm and $\beta=122.09°$) is closely related to the tunneled structure of Ga_4TiO_8 ($x=y=0$) [7–10]. The conductivity (σ) of Na^+ ions within the tunnels has been much higher along the tunnel direction, which is parallel to the *b*-axis, than perpendicular to this direction. At 573 K, the σ-value of the former direction was 1×10^{-2} S/cm, which is ca. 2000 times higher than that of the latter. The activation energy of conduction along the *b*-axis was 0.25 eV (temperature range 298–723 K). Edwards et al. [8] have examined the temperature dependence of σ for the randomly grain-oriented polycrystalline $Na_{0.7}Ti_{0.3}Ga_{4.7}O_8$. The σ-value increased steadily from ca. 1×10^{-7} to 1×10^{-3} S/cm as the temperature increases from 573 to 1273 K. At 573 K, the σ-value was lower by a factor of 10^5 than that along the *b*-axis of the single crystal. Thus, the *b*-axis-oriented crystallization would be indispensable for the NTGO polycrystalline materials for the sake of high ionic conductivity.

Sintered polycrystals synthesized by normal sintering methods generally possess a randomly oriented grain structure and isotropic mechanical (e.g., bending strength and fracture toughness) and physical (e.g., thermoelectric, piezoelectric, pyroelectric, and magnetic) properties. In recent years, a facile and novel technique utilizing reactive diffusion has made it possible to produce the well-aligned polycrystals of lanthanum silicate oxyapatite (LSO) [11–15]. Because LSO is characterized by the much higher conductivity of oxide ions parallel to the *c*-axis than perpendicular to this direction [16–18], the grain-aligned polycrystalline materials have shown relatively high oxide-ion conductivity along the common *c*-axis.

In the present study, we focused on the preparation of highly *b*-axis-oriented polycrystalline NTGO because of the much higher σ-value along the grain-alignment direction than perpendicular to this direction. Actually, we successfully prepared the grain-aligned

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polycrystalline NTGO embedded in Ga_2O_3-doped $Na_2Ti_4O_9$ matrix by the reactive diffusion technique. The chemical composition as well as the crystal structure of NTGO were determined by X-ray diffractometry. The Na-deficiency in crystal structure probably contributed to the relatively high ionic conductivity parallel to the *b*-axis.

2. Experimental

2.1. Materials

Two kinds of powder specimens of Ga_2TiO_5 and $NaGaO_2$ were prepared from reagent-grade chemicals of Ga_2O_3 (99.99%, Kishida Chemicals Co. Ltd., Osaka, Japan), TiO_2 (99.5%, Kishida Chemical Co. Ltd., Osaka, Japan) and Na_2CO_3 (99.5%, Kishida Chemical Co. Ltd., Osaka, Japan). Individual well-mixed chemicals with the desired chemical compositions were heated at 1673 K for 8 h, followed by quenching in air. The reaction products were slightly sintered polycrystalline materials. They were ground to obtain fine powder specimens.

We prepared sandwich-type diffusion couples of Ga_2TiO_5/$NaGaO_2$/Ga_2TiO_5. Each of the couples was made up of two Ga_2TiO_5 pellets (0.200 g each) with the size of φ13 mm × 0.30 mm and one $NaGaO_2$ pellet (0.250 g) with the size of φ13 mm × 0.48 mm, hence the bulk chemical composition was 20.1 mol% Na_2O, 29.9 mol% TiO_2 and 50.0 mol% Ga_2O_3. After the preliminary heating experiment at 1423–1223 K, they were heated at the optimum temperature of 1323 K for 24 h, and then slowly cooled to ambient temperature at ~300 K/h.

2.2. Characterization

We cut the annealed couples using a diamond saw and exposed the sections, the surfaces of which were perpendicular to or parallel to the former Ga_2TiO_5/$NaGaO_2$ interfacial contact boundaries. These cross-sections were subsequently ground with 800-grid SiC paper and finally polished with 1-μm diamond paste. The microtexture on the polished surface was observed using a scanning electron microscope (SEM; JSM-6010LA, JEOL Ltd., Tokyo, Japan).

X-ray diffraction (XRD) intensities were collected on the polished section surface using a powder diffractometer (X′Pert PRO Alpha-1, PANalytical B.V., Almelo, The Netherlands) equipped with an incident-beam Ge(111) Johansson monochromator to obtain Cu*K*α$_1$ radiation and a high-speed detector. We used a programmable divergence slit to keep a constant length of 5 mm for the illuminated specimen surface. The beam width was 5 mm, hence the analyzed surface area was ca. 25 mm^2 regardless of the 2θ value with $10.0^\circ \le 2\theta \le 90.0^\circ$. We used the Lotgering method [19] to estimate the texture fraction of the NTGO {0*k*0} planes from the XRD pattern. The Lotgering factor f_{0k0} is defined as the fraction of area textured with the crystallographic plane of interest using the formula

$$f_{0k0}=(P_{0k0}-P_0)/(1-P_0)$$

where

$$P_{0k0}=(\Sigma I_{0k0})/(\Sigma I_{hkl})$$

and

$$P_0=(\Sigma I_{0k0}{}^0)/(\Sigma I_{hkl}{}^0)$$

where I_{hkl} and $I_{hkl}{}^0$ are the integrated intensities of *hkl* reflections for, respectively, the textured specimen and the randomly grain oriented one. We examined the whole XRD pattern by the Le Bail method [20] and extracted the I_{hkl}-values using a computer program RIETAN-FP [21]. The $I_{hkl}{}^0$-values were generated from calculation, using the same computer program, for the NTGO polycrystal with random grain orientation.

We ground one of the annealed sandwich-type diffusion couples (ca. 1.3 mm in thickness) using 800-grid SiC paper and eventually polished using 1-μm diamond paste to obtain the thin-plate electrolyte. Electrodes were prepared by coating opposite plate faces with a platinum paste and subsequent heating at 1073 K to decompose the paste and harden the Pt residue. We collected the impedance spectroscopy data in the range of 4 Hz–5 MHz during the heating process from 573 K to 1073 K in air using an impedance analyzer (model 3570, HIOKI E.E. Co., Nagano, Japan). A nonlinear least square fitting method using a ZView software was employed to analyze the equivalent circuits [22].

We picked up a needle-like microcrystal (approximately 45 μm × 10 μm × 5 μm) of NTGO from the crushed thin-plate electrolyte and mounted it on the end of a soda glass capillary. Single-crystal XRD data were obtained on a Bruker Smart Apex II diffractometer using Mo*K*α radiation (50 kV and 35 mA). We refined the unit-cell parameters and extracted the observed structure factors using a program package Apex2-W2K/NT [23]. The initial structural model was derived by the charge flipping method [24] on a computer program JANA2006 [25], and the structural parameters were refined subsequently by the program. We standardized the structural data according to the formulated rules by Parthé and Gelato [26] using a computer program STRUCTURE TIDY [27]. For the evaluation of the anharmonicity, the Gram–Charlier expansion up to the third-rank tensor was applied to the atomic displacement parameters (ADPs) of Na site after the refinement of the harmonic displacement model [28]. We validated the significance of the final structural model by the difference Fourier maps that were obtained using the JANA2006 program. The crystal structure model was visualized with a computer program VESTA [29]. The data collection and refinement parameters are summarized in Table 1.

The powder specimen of the crushed thin-plate electrolyte was deposited with ethyl alcohol on a copper grid coated with holy

Table 1
Summary of data collection and refinement parameters for $Na_{0.85}Ti_{0.51}Ga_{4.37}O_8$ (NTGO).

Chemical composition	$Na_{0.850(14)}Ti_{0.511(8)}Ga_{4.369(13)}O_8$
Space group	*C*2/*m* (No.12)
a/nm	1.23463(3)
b/nm	0.29855(1)
c/nm	0.94088(2)
β/deg	122.566(1)
V/nm^3	0.292279(14)
Z	2
Formula weight	476.59
D_x/Mgm^{-3}	5.4136(3)
Crystal color	Clear
Crystal form	Rectangular
Crystal size/μm	Approximately 45 × 10 × 5
μ/mm^{-1}	20.623
Diffractometer	Bruker Smart ApexII
Radation type	Mo *K*α
Wavelength/nm	0.071073
Temperature/K	298
θ_{max}/deg	29.985
Collection range	$-16 \le h \le 15$ $-4 \le k \le 4$ $-13 \le l \le 13$
No. of measured reflections	5969
No. of unique reflections	503
No. of observed reflections [$F^2 > 3\sigma(F^2)$]	440
R_{int}	0.0193
R	0.0205
wR	0.0282
S	1.97
No. of parameters	57
$\Delta\rho_{max}$/1000 nm^{-3}	0.56
$\Delta\rho_{min}$/1000 nm^{-3}	−0.66