FULL PAPER

Microstructural effects on sodium ion conduction properties of grains and grain boundaries of $\text{Na}_5\text{YSi}_4\text{O}_{12}$ -type silicophosphate glass-ceramics

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We studied the effects of crystallization conditions on the conduction properties of the $\text{Na}_5\text{YSi}_4\text{O}_{12}$ -type sodium ion conducting glass-ceramics. Crystallization process was controlled by varying annealing parameters of nucleation time (0–200 h) and crystal growth temperature (900–1100 °C). The present results showed that a shorter nucleation time with annealing at 900 °C for crystal growth gave rise to higher conductivities of $5 \times 10^{-2} \text{ S cm}^{-1}$ at representative temperatures of 300 °C and $3 \times 10^{-3} \text{ S cm}^{-1}$ at 150 °C, respectively. Those results were attributed to the microstructures of glass-ceramics and the conductivities of a whole glass-ceramic were considered to be dominated by those of grains at 300 °C and, on the other hand, strongly influenced by those of grain boundaries at 150 °C. It was found that the dependence of a whole conductivity on the apparent number of grain boundaries calculated as the ratio of a whole thickness to an average grain diameter was stronger in the measurements at 150 °C than at 300 °C. Considering the result, we propose the use of largely grained glass-ceramics for both higher and lower temperature uses.

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1. Introduction

All solid-state ion batteries (ASSB) are considered as the future key device to provide clean energy for environmental issues. Above all, lithium ion batteries have been the main target for ASSB, however, sodium ion batteries are also desired to realize because of the natural resources much more abundant than lithium-containing minerals.¹⁾ Sodium sulfides solid electrolytes have recently gathered much attention as the leading device of sodium ASSB.^{2),3)} Considering the instability of the sulfides in an oxidizing atmosphere, however, sodium ion conducting oxides are also becoming a current target for sodium ASSB as a next generation device^{4)–14)} in addition to high-temperature uses such as Na/S batteries.

The β/β'' -alumina¹⁵⁾ and NASICON¹⁶⁾ have been conventionally recognized as the practical Na^+ conducting oxides with 10^{-1} – 10^{-2} and 10^{-4} – $10^{-5} \text{ S cm}^{-1}$ at 300 and 25 °C, respectively, and to date, numerous studies have

been carried out on those Na^+ conducting ceramics. Subsequently to those, rare-earth (R) containing sodium silicates of $\text{Na}_5\text{RSi}_4\text{O}_{12}$ were discovered as the Na^+ conducting compound comprised of SiO_4^{4-} -12 membered-rings skeleton structure.^{17)–19)} Recently, $\text{Na}_2\text{M}_2\text{TeO}_6$ (M: Ni, Co, Zn, Mg)^{20)–22)} has been found to exhibit fast Na^+ ion conductivities of 10^{-2} and $10^{-4} \text{ S cm}^{-1}$ at the respective temperatures of 300 and 25 °C. All of these are produced as polycrystalline conductors by sintering of compressed powders. Contrastingly, we have developed glass-ceramic Na^+ conductors according to $\text{Na}_5\text{RSi}_4\text{O}_{12}$ -based silicophosphates because of tractability of forming, to which the partial replacement of PO_4^{3-} for the SiO_4^{4-} -skeleton contributes due to lowering melting point of starting glasses. The production of dense tubes is inevitable for Na/S batteries, where glass-making processing can be expected to have an advantage over conventional sintering.^{5)–7)} To date, we have developed the dense glass-ceramics in the systems of $\text{Na}_5\text{RSi}_4\text{O}_{12}$ (R: various rare-earth elements),²³⁾ $\text{Na}_5\text{YSi}_4\text{O}_{12}$ -type $\text{Na}_{3+3x-y}\text{Y}_{1-x}\text{P}_y\text{Si}_{3-y}\text{O}_9$,^{24)–33)} $\text{Na}_5\text{FeSi}_4\text{O}_{12}$,³⁴⁾ and the derivatives $\text{Na}_{5-z}\text{Fe}_{1-z}\text{M}_z\text{Si}_4\text{O}_{12}$ (M: Al, Ga, B),³⁵⁾ and $\text{Na}_5\text{ZrSi}_4\text{O}_{12}$.³⁴⁾

Of those $\text{Na}_5\text{YSi}_4\text{O}_{12}$ family, the most conductive materials and tractable glass-ceramics with the composi-

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tion of $\text{Na}_5\text{YSi}_4\text{O}_{12}$ -type $\text{Na}_4\text{Y}_{0.6}\text{P}_{0.2}\text{Si}_{3.8}\text{O}_9$ was taken in this study. The whole conduction properties of glass-ceramics primarily depend on those of crystallized grains at a higher temperature, whereas the characteristics of grain boundaries have considerable influence on the total conductivities. Because of the high density of more than 98 %, a porosity effect was neglected in this study. The microstructure comprising grain and grain boundaries can be controlled through the thermal process of crystallization and grain growth. With the aim at the development of Na^+ conducting glass-ceramics for both Na/S batteries for high- and ASSB for low-temperature uses, the present study focused on the microstructural effects on the conduction properties of glass-ceramic $\text{Na}_4\text{Y}_{0.6}\text{P}_{0.2}\text{Si}_{3.8}\text{O}_9$ produced under various temperature and time for crystallization and grain growth.

2. Materials and methods

2.1 Glass-making, and -crystallization procedure

The precursor glasses were produced according to the previous reports.^{34),35)} For clarity, the summarized procedure was introduced in the following; the starting powders were prepared by mechanical mixture of the reagent-grade powders of anhydrous Na_2CO_3 , Y_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and SiO_2 according to the chemical formula of $\text{Na}_4\text{Y}_{0.6}\text{P}_{0.2}\text{Si}_{3.8}\text{O}_9$, and calcined at 900 °C for 0.5 h, then melted at 1350 °C for 1 h. The composition will be referred to as NYPS in the following for convenience. The melts were rapidly poured into a cylindrical graphite with the size of 15 mm diameter for electrical measurements, followed by annealing at 500 °C for 3 h to form precursor glasses. This study focused on the effects of nucleation time (t_N) and crystallization temperature (T_{CG}) on conduction properties, because the microstructural evolution of glass-ceramics depends on both t_N and T_{CG} . The annealing process was carried out under the controlled schedule shown in Fig. 1 according to the previously reported results on differential thermal analyses.^{34),35)} Precursor glasses were annealed for nucleation at 600 °C for 6 h, above approximately 50 °C of the glass transition point, for various t_N of 0 to 200 h, thereafter heated to the temperature of T_{CG} for crystal

Fig. 1. Heating schedule from room temperature through 600 °C for nucleation to T_{CG} for crystal growth with a heating rate of 60 °C/h (a-b, c-d) and time of 0–200 h (b-c) and 5 h (d-e).

growth, where T_{CG} was chosen from 900 to 1100 °C for 5 h, because less conductive precursor phases of $\text{Na}_3\text{YSi}_3\text{O}_9$ and/or $\text{Na}_9\text{YSi}_6\text{O}_{18}$ appear at lower temperatures than 900 °C.²⁸⁾ Thus obtained glass and glass-ceramic specimens were polished with 0.5 μm diamond paste, thereafter subjected to the conductivity measurements.

Identification of the crystalline phases were performed on crushed powders of crystallized specimens by X-ray diffraction (XRD) method. Scanning electron micrographic (SEM) observation was also performed on bulk samples chemically etched with HF solution to evaluate the microstructure and average grain-sizes (D). The apparent densities of glass ceramics were measured by the Archimedes method using kerosene as immersion solution.

2.2 Electrical measurements

To evaluate ionic conductivities, the complex impedance measurements were done on cylindrical glasses and glass-ceramics of typically 15 mm in diameter and 2 mm in thickness. Thin films of Au were deposited as electrodes on those polished surfaces by rf-magnetron sputtering, and the ac fields ranging from 5 Hz to 10 MHz in frequency were applied to the glass and glass-ceramic samples for the measurements of conductivities (σ) at the temperatures of 150 to 350 °C, because of our limited measuring facility. The complex impedance or admittance loci of glass and glass-ceramics were analyzed by the universal equivalent circuit,^{32)–35)} which was experimentally found to comprise 2 semi-circles in any present glass-ceramic. The two intercepting points of the semi-circles on the real axis are interpreted as the conductance of crystallized grains (σ_G), and the total conductance (σ_{Total}) of grains and grain boundaries (σ_{GB}).

3. Results

3.1 Characterization of crystallized glass by XRD and SEM

As shown in Fig. 2, powder XRD analyses indicated all the observed diffraction peaks marked with solid circles were consistent with those listed in ICDD data, confirming

Fig. 2. XRD patterns of glasses crystallized at 900 °C (a), 950 °C (b), 1000 °C (c), 1050 °C (d), and 1100 °C (e), where solid marks correspond to the peaks belonging to $\text{Na}_5\text{YSi}_4\text{O}_{12}$ -type diffraction.

that all of the glass-ceramic samples crystallized at temperatures T_{CG} of 900 to 1100 °C were consisted of Na₅YSi₄O₁₂-type single phase.

All the specimens were confirmed by the Archimedes method to have apparent densities of more than 98 %. Scanning electron micrographs shown in **Fig. 3** represent the microstructural evolution with t_N , and the average grain size (D) varied from ca. 3 to 8 μm . As the thickness of a glass-ceramic sample was 2 mm, the number of grain boundaries was estimated as $2 \times 10^3/D$ to vary from almost 2×10^2 to 7×10^2 , depending on t_N and T_{CG} .

3.2 Dependence of conductivity on crystal growth temperature

The typical examples of complex admittance diagrams

Fig. 3. Scanning electron micrographs of glasses annealed at 600 °C for various nucleation time (t_N) and crystallized at 1100 °C for 5 h, where the inserted figures show the time of t_N .

of the glass-ceramic NYPS specimens (nucleation at 600 °C for 6 h) are shown in **Figs. 4(a1–a3)** and **4(b1–b3)**. The equivalent circuit according to the previous report³⁶⁾ was applied to the analysis of those measured admittance diagrams, which consisted of two semi-circles at all the measuring temperatures. Using the two intercepting points of Y_1 and Y_2 on the real axis, the conductivities through grains (σ_G) and grain boundaries (σ_{GB}), and the total conductivity of a sample (σ_{Total}) with the dimension of S cm^{-1} were calculated using the geometrical parameters of a surface area ($S = 1.5 \text{ cm}^2$) and a thickness ($L = 0.2 \text{ cm}$) as follows:

$$\sigma_{Total} = kY_1, \quad \sigma_G = kY_2, \quad \sigma_{GB} = kY_1Y_2/(Y_2 - Y_1),$$

$$\text{where } k = S/L = 7.5 \text{ cm.}$$

Because of the complexity of grain boundary geometry, the same geometrical factor $k = 7.5 \text{ cm}$ was conveniently employed for the calculation of all of σ_{Total} , σ_G , and σ_{GB} . Using the temperature dependence of those conductivities, the activation energies (E) of sodium ion conduction were calculated from the Arrhenius plots for the total (E_{Total}), grains (E_G) and grain boundaries (E_{GB}). As seen from the figures, the difference between Y_2 and Y_1 became much smaller at 300 °C [Figs. 4(a3) and 4(b3)] than 150 °C [Figs. 4(a2) and 4(b2)] in both samples crystallized at T_{CG} of 900 and 1100 °C. The effect of the temperature T_{CG} (nucleation at 600 °C for 6 h) on the conductivities measured at 300 °C are shown in **Fig. 5**, indicating $\sigma_G \cong \sigma_{Total}$ ranging from 1.5×10^{-2} to $2.5 \times 10^{-2} \text{ S cm}^{-1}$ with almost constant E_G and E_{Total} of ca. 30 and 35 kJ mol^{-1} , respectively, independently of T_{CG} , and the apparent values of σ_{GB} were between 2.8×10^{-1} and $0.8 \times 10^{-1} \text{ S cm}^{-1}$ with

Fig. 4. Complex admittances of glass-ceramics crystallized at 900 °C (a1) and 1100 °C (b1) (nucleation at 600 °C for 6 h) measured at temperatures from 150 to 350 °C, where the results obtained at 150 °C (a2, b2) and 300 °C (a3, b3) are shown as typical examples for comparison. The symbols Y_1 and Y_2 represent the intercepting points of the two admittance arcs on the real axis, corresponding to the total conductivity of a sample (σ_{Total}) and the conductivity through grains (σ_G), respectively.

E_{GB} varying from 36 to 100 kJ mol⁻¹ with increasing T_{CG} . It is noted here that higher values of σ_{GB} arose from the use of the apparent value of k for grain boundary geometry, and the actual one should be much larger than 7.5 because of almost numerous S against extremely small L .

As the highest σ_{Total} was obtained at T_{CG} of 900 °C, the effect of nucleation time t_N was evaluated at T_{CG} of 900 °C, where t_N was changed from 0 to 200 h. Some examples of the obtained conductivities are shown in the Arrhenius plots (Fig. 6) for $t_N = 0$ (a), 6 h (b), 50 h (c), and 200 h (d), indicating that the lines of σ_G and σ_{GB} crossed each other and the intersecting points went up to higher temperatures with increasing t_N .

To investigate the effect of t_N on conduction properties, the demonstrative examples of σ obtained at high (300 °C) and low temperatures (150 °C) with E are summarized in Figs. 7(a)–7(d). The value of a whole conductivity σ_{Total} at 300 °C varied from 5×10^{-2} down to 0.8×10^{-2} S cm⁻¹ with increasing t_N [Fig. 7(a)]. The similar tendency was

Fig. 5. Dependence of conductivities at 300 °C of grains (G), grain boundaries (GB), and the total (Total) on crystallization temperature (nucleation at 600 °C for 6 h).

observed in the dependence of σ_G on t_N [Fig. 7(b)], because the relation of $\sigma_G \cong \sigma_{Total}$ holds at higher temperatures, as was mentioned above. To the contrary, the values of σ_{Total} at 150 °C varied within the limited range of 10^2 S cm⁻¹ from 3×10^{-3} down to 2×10^{-5} S cm⁻¹ with increasing t_N [Fig. 7(a)], while σ_G at 150 °C varied within the narrow-limited range of 1×10^{-2} down to 4×10^{-3} S cm⁻¹ with increasing t_N [Fig. 7(b)]. On the other hand, the values of σ_{GB} both at 300 and 150 °C drastically decreased between $t_N = 2$ and 50 h and then gradually reached to almost constant [Fig. 7(c)]. The change of σ_{GB} at 150 °C was scattering in the range of 10^3 S cm⁻¹, more largely than that of σ_{GB} at 300 °C. The conduction activation energies (E) for grains were almost constant as

Fig. 6. Arrhenius plots of glass-ceramics nucleated at 600 °C for 0 h (a), 6 h (b), 50 h (c), and 200 h (d), thereafter crystallized at 1100 °C for 6 h.

Fig. 7. Nucleation time (t_N) dependence of conductivities of the total (σ_{Total}) (a), grains (σ_G) (b), grain boundaries (σ_{GB}) (c), obtained at 150 and 300 °C, and the activation energies (E) of grains (G) and grain boundaries (GB) (d). The glass-ceramic specimens were prepared by crystallization of nucleated glasses at 1100 °C for 6 h.

36 kJ mol⁻¹, whereas those for grain boundaries were scattered between 70 and 110 kJ mol⁻¹ [Fig. 7(d)], consistent with previously reported values of silicophosphate glass-ceramics.²⁸⁾ The higher values of E for grain boundaries than those for grains indicate the inferiority of the conduction through grain boundaries in comparison with that through grains.

4. Discussion

According to the previous studies on glass-ceramic engineering, annealing time (t_N) long enough for homogeneous nucleation generally results in small grained polycrystalline, whereas shorter t_N gives largely grained ones after heating at a temperature for crystal growth (T_{CG}).^{37)–39)} The developed microstructures of crystallized glasses are schematically depicted for comparison with each other in Fig. 8, indicating that crystallized grains grow larger in a glass with fewer nuclei than those in a densely nucleated glass. As mentioned above, the grain-sizes (D) of glass ceramic samples were ranging from 8 down to 3 μ m with increasing t_N , and as the common thickness of glass-ceramic samples were fixed as 2 mm, the apparent number of grain boundaries (n_{GB}) can be estimated as $n_{GB} = \text{thickness} (\mu\text{m}) / \text{grain diameter} (\mu\text{m}) = 2 \times 10^3 / D$. The calculated values of n_{GB} varied from 1.2×10^2 to 3.2×10^2 , with which the total conductivities of glass-ceramic samples were plotted against the average values of D (Fig. 9). The figure shows the dependence of σ_{Total} on n_{GB} , expressed as the slope of $(\log \sigma_{\text{Total}}) / n_{GB}$, was stronger in the measurements at 150 °C than at 300 °C, supporting the exclusive role of grain boundaries at lower temperatures in the total conductivity. It is also noted that the slope obtained (Δ_1) at 150 °C was rather steeper at $n_{GB} < 220$ than that (Δ_2) at $250 < n_{GB}$. In case of a uniformly constant conductivity of grain boundaries independent of grain-size, the slopes of Δ_1 and Δ_2 must be equal to each other, indicating that the property of grain boundaries can be changed in the process of grain growth. To clarify the change, we introduce a parameter of α , which is defined as the resistance of a single grain layer (R_{SGB}) enclosed with grain

boundaries, since $R_{SGB} \propto R_{\text{Total}} / n_{GB} = (1 / \sigma_{\text{Total}}) \times (L / S) / (L / D) = D / (S \times \sigma_{\text{Total}}) (\Omega)$. The values of α were summarized in Table 1 and the relationship between R_{SGB} and D is shown in Fig. 10, where the values of $R_{SGB} = (D / \sigma_{\text{Total}})$ slightly varied within 2×10^2 to $9 \times 10^2 \Omega$, regardless of D at 300 °C. On the other hand, the values obtained at 150 °C were almost constant around 1×10^5 to $2 \times 10^5 \Omega$ for

Fig. 9. Dependence of the total conductivities (σ_{Total}) measured at 150 and 300 °C on number of grain boundaries (n_{GB}) along thickness, where the parameters Δ_1 and Δ_2 represent the slopes of $(\log \sigma_{\text{Total}}) / n_{GB}$, depending on the region of n_{GB} .

Table 1. Effect of nucleation time on grain size (D) and resistivity along a single grain boundary (R_{SGB}) measured at 150 and 300 °C

Nucleation Time [h]	D [μ m]	R_{SGB} [Ω]	
		150 °C	300 °C
0	7.6	3×10^3	2×10^2
2	6.8	5×10^3	3×10^2
3	5.9	7×10^3	2×10^2
6	6.5	8×10^4	4×10^2
25	3.5	8×10^4	6×10^2
50	3.7	1×10^5	8×10^2
100	4.8	2×10^5	9×10^2
150	3.2	2×10^5	7×10^2
200	3.3	1×10^5	7×10^2

Fig. 8. Schematic microstructural evolution of glass during crystallization, where patterns A and B correspond to nucleation treatment for short and long time, respectively.

Fig. 10. Dependence of resistivity along a single grain boundary (R_{SGB}) measured at 150 and 300 °C on grain size.

$D < 5\ \mu\text{m}$, whereas those were scattered roughly between 3×10^3 to $8 \times 10^4\ \Omega$ for $5\ \mu\text{m} < D$. Those results indicate the crystallinity, volume, or composition of grain boundaries can change during grain growth depending on the initial size and density of nuclei, in spite of the annealing for crystallization at the same temperature of $900\ ^\circ\text{C}$. As mentioned above (Fig. 8), the short-time annealing for nucleation gave rise to larger grained glass-ceramics after crystallization. The depicted figure also suggests that grain boundaries might be promoted to crystallize in a densely nucleated glass because the homogeneous structure. Control of annealing schedule of glasses can be said to be important for the preparation of conductive glass-ceramics at lower temperature.

5. Conclusion

We have studied the effects of annealing conditions of nucleation time (0–200 h) and crystal growth temperature (900 – $1100\ ^\circ\text{C}$) on the conductivity of $\text{Na}_5\text{RSi}_4\text{O}_{12}$ -type Na^+ ion conducting glass-ceramics. A shorter nucleation time with annealing at $900\ ^\circ\text{C}$ for crystal growth gave rise to the highest conductivities of $5 \times 10^{-2}\ \text{S cm}^{-1}$ at $300\ ^\circ\text{C}$ and $3 \times 10^{-3}\ \text{S cm}^{-1}$ at $150\ ^\circ\text{C}$, respectively. The results were attributed to the fact that the conductivities of a whole glass-ceramic were dominated by those of grains at high temperatures such as $300\ ^\circ\text{C}$ and, on the other hand, strongly influenced by those of grain boundaries at lower temperature of $150\ ^\circ\text{C}$.

Based on the present results, the annealing conditions of time and temperature should be appropriately chosen for the high- and low-temperature uses such as sodium/sulfur- and all-solid state-secondary batteries.

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