FULL PAPER

Effects of boron and phosphorus substitution on sodium-ion conduction properties of glass-ceramic Na$_5$FeSi$_4$O$_{12}$

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This study has focused on the effect of Si-substitution with alio-valent boron and phosphorus on sodium-ion (Na$^+$) conduction properties of the newly developed glass-ceramic Na$_5$FeSi$_4$O$_{12}$. The glass-ceramics with the Na$^+$ conducting single phase were obtained with the compositions Na$_{5+x}$Fe$_{3-x}$Si$_{4-y}$O$_{12}$ and Na$_{5-y}$Fe$_{y}$P$_{y}$Si$_{4-y}$O$_{12}$, although the solubility limits were restricted as $x < 0.4$ and $y < 0.3$. The conductivity of the mother Na$_5$FeSi$_4$O$_{12}$ glass-ceramics was enhanced on both Na$_{5+x}$Fe$_{3-x}$Si$_{4-y}$O$_{12}$ and Na$_{5-y}$Fe$_{y}$P$_{y}$Si$_{4-y}$O$_{12}$, and the maximum conductivities were achieved on the compositions Na$_{5.3}$Fe$_{2}$Si$_{3.8}$O$_{12}$ ($x = 0.2$) and Na$_{4.8}$Fe$_{0.1}$Si$_{3.9}$O$_{12}$ ($y = 0.1$), as high as $3.1 \times 10^{-3}$ and $4.2 \times 10^{-3}$ S cm$^{-1}$ at 300 °C, respectively.

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1. Introduction

Sodium-ion (Na$^+$) conductive solid electrolyte is a highly potential candidate for all solid state batteries. Sulphide-based batteries were firstly developed for this purpose.$^{1-5}$ Oxide-based ceramic materials are also the focus of current research because of the excellent chemical stability in addition to the high ionic conductivity.

The present authors have developed Na$^+$ conductors of sodium rare-earth silicophosphates using the compositional formula Na$_5$FeSi$_4$O$_{12}$. As the preliminary investigation for improvement of conduction properties of Na$_5$FeSi$_4$O$_{12}$, we examined the materials with the composition of Na$_{5+x}$Fe$_{3-x}$Si$_{4-y}$O$_{12}$, in which 14th group Si was partially replaced with 13th group elements (M) of boron (B), Al, Ga or phosphorus (P) in the periodic table. These materials were made by crystallization of the starting glasses. In this preliminary study using the fixed value of $x = 0.1$, the conductivity was enhanced from $1.3 \times 10^{-3}$ to $1.7 \times 10^{-3}$ S cm$^{-1}$ at 300 °C in B-substituting glass-ceramics of Na$_{5.1}$Fe$_{0.1}$Si$_{3.9}$O$_{12}$.

Based on the results, we have explored more conductive Na$_5$FeSi$_4$O$_{12}$-based glass-ceramics according to the formula Na$_{5+x}$Fe$_{3-x}$Si$_{4-y}$O$_{12}$. Phosphorus-incorporated Na$_5$FeSi$_4$O$_{12}$-type glass-ceramics were also studied using the compositional formula Na$_{5-y}$Fe$_{y}$P$_{y}$Si$_{4-y}$O$_{12}$, because 15th group P was experimentally found to partially substitute Si in the previous study.$^{6-8}$ The effects of B and P on the phase formation, the microstructure, and the conduction properties of glass-ceramics were also investigated.

2. Materials and experimental methods

To investigate the limited solubility ranges to form complete solid solutions, the parameters $x$ and $y$ were changed

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between 0 and 0.5 according to the compositions of Na$_5$+$_x$FeB$_x$Si$_{4-x}$O$_{12}$ and Na$_5$-$_y$FeP$_y$Si$_{4-y}$O$_{12}$ in this study. The starting glasses were made according to the preliminary work. The starting reagents were the powders of anhydrous Na$_2$CO$_3$ (FUJIFILM Wako Pure Chemical Corp., 99.8\% pure), Fe$_2$O$_3$ (FUJIFILM Wako Pure Chemical Corp., 95.0\% pure), H$_3$BO$_3$ (FUJIFILM Wako Pure Chemical Corp., 99.5\% pure), NH$_4$H$_2$PO$_4$ (FUJIFILM Wako Pure Chemical Corp., 95.0\% pure), and SiO$_2$ (FUJIFILM Wako Pure Chemical Corp., 99.9\% pure). The mixed powders were melted at 1350 °C for 1 h after calcination at 900 °C for 1 h, then melted to form cylindrical-shaped glasses.

The glass transition temperature (T$_g$) had been determined by differential thermal analysis (DTA). The quenched glasses were annealed for several hours at the optimum temperatures of 25 °C below T$_g$ to release internal stress. According to the previous report, the bulk glasses were pre-treated by heating up to a temperature above ca. 50 °C of T$_g$ for homogeneous nucleation. These annealed glasses were heated at 700 °C for 5 h for crystallization. Crystallized bulks were crushed into powders for X-ray diffraction (XRD) analysis, the results of which were subjected to the calculation of the hexagonal lattice constants as well as phase confirmation. The microstructural observation by the scanning electron microscopy (SEM) was done for the evaluation of gran size. Ionic conductivities were measured by the alternating current (AC) two-probe method on sintered glass-ceramics with typical 14 mm in diameter and 2 mm in thickness. Sputtered Au on the polished surfaces was used as electrodes. The applied AC field ranged from 40 to 100 MHz in frequency. The temperature dependence of the conductivity was measured similarly at several temperatures ranging from room temperature to 350°C. Na$^+$ ion transference numbers of the glass-ceramics were determined by the Wagner polarization method. Electronic conductivities were measured by the direct current two-probe method with a potentiostat. Using these results, the ionic conductivity was estimated.

### Table 1. DTA thermal properties of Na$_5$FeSi$_4$O$_{12}$, Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_4$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$ glasses

|                | $T_g$/°C | $T_d$/°C | $T_c1$/°C | $T_m$/°C |
|----------------|----------|----------|-----------|----------|
| Na$_5$FeSi$_4$O$_{12}$ | 424      | 558      | 727       | 841      |
| Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$ | 446      | 617      | 670       | 825      |
| Na$_4$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$ | 467      | 627      | 706       | 828      |

### 3. Results and discussion

#### 3.1 XRD measurement and DTA of precursor glass

All the specimens of precursor Na$_5$FeSi$_4$O$_{12}$, Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_5$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$ after quenching of the melts were confirmed to be amorphous by XRD analyses. Table 1 summarizes the temperatures of glass transition (T$_g$), crystallization (T$_c$), and melting (T$_m$), read from the DTA curves, for those three produced precursor glasses (Fig. 2). Regarding the crystallization temperatures on Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_5$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$, the observed two peaks were assigned to T$_c1$ and T$_c2$ according to the previous study. The nucleation temperature was set at 30 °C higher than T$_g$, and the nucleus growth temperature was set at the melting points from the crystallization temperature (T$_c2$) on the high temperature side.

#### 3.2 Crystalline phases and lattice parameters of glass-ceramics

XRD patterns of the typical 3 glass-ceramic specimens of Na$_5$FeSi$_4$O$_{12}$, Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_5$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$ were confirmed to be identical to that of International Centre for Diffraction Data (ICDD) of Na$_5$FeSi$_4$O$_{12}$ (Fig. 3). Thus the glass-ceramics with Na$_5$FeSi$_4$O$_{12}$-type single-phase were obtained for the parameter $x$ between 0 and 0.3 in Na$_5$.FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and the mixed phases of Na$_5$FeSi$_4$O$_{12}$ with Na$_2$SiO$_3$ were formed in the range of 0.4 < $x$ < 0.5. Most specimens were crack-free glass-ceramics. On Na$_5$.FeP$_{0.1}$Si$_{3.9}$O$_{12}$, the single phase was attained in the range of $y$ < 0.3. Using the specimens with...
the single phase, the changes of the lattice parameters were evaluated with compositional change of $x$ and $y$; both $a$ and $c$ constants decreased with increasing B and P substitutes (Table 2). The shrinkage of $a$- and $c$-axes by substitution with B or P is reasonably attributed to the difference in the ionic sizes of tetrahedral (SiO$_4$)$^{4-}$ with (BO$_4$)$^{5-}$ and (PO$_4$)$^{3-}$. The deficient or excess sodium ions for charge compensation can be also attributable to the changes in lattice parameters.

Microstructural factors such as sizes of grains and pores and number of grainboundaries along thickness, and pore volume sometimes have important roles in ionic conduction. From the microstructure observed by SEM, all the specimens had apparent densities of more than 98%, and the average grain sizes were 1–5 µm on glass-ceramics Na$_5$FeSi$_4$O$_{12}$ [Figs. 4(a) and 4(b)] and Na$_5.2$FeB$_{0.2}$Si$_{3.8}$O$_{12}$, Table 2. Lattice constants of Na$_5$FeSi$_4$O$_{12}$, Na$_{5.1}$FeB$_{0.1}$Si$_{3.9}$O$_{12}$, and Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$ glass-ceramics

| Lattice parameters | $a = b$/nm | $\Delta a = \Delta b$/nm | $c$/nm | $\Delta c$/nm |
|--------------------|------------|--------------------------|--------|--------------|
| Na$_5$FeSi$_4$O$_{12}$ | 2.1410 | 0.0006 | 1.2284 | 0.0004 |
| Na$_{5.1}$FeB$_{0.1}$Si$_{3.9}$O$_{12}$ | 2.1387 | 0.0007 | 1.2274 | 0.0004 |
| Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$ | 2.1373 | 0.0007 | 1.2272 | 0.0004 |
| Na$_{5.3}$FeB$_{0.3}$Si$_{3.7}$O$_{12}$ | 2.1374 | 0.0014 | 1.2262 | 0.0009 |
| Na$_{5.4}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$ | 2.1389 | 0.0005 | 1.2292 | 0.0003 |
| Na$_{5.5}$FeP$_{0.2}$Si$_{3.8}$O$_{12}$ | 2.1398 | 0.0009 | 1.2288 | 0.0006 |

Fig. 2. DTA curves for Na$_5$FeSi$_4$O$_{12}$, Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_{5.3}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$ glasses.

Fig. 3. XRD patterns for Na$_5$FeSi$_4$O$_{12}$, Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$, and Na$_{5.3}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$ glass-ceramics.

Fig. 4. SEM photographs of the microstructures of Na$_5$FeSi$_4$O$_{12}$ (a), Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$ (b), and Na$_{5.3}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$ (c) glass-ceramics.
and 5–10 μm on glass-ceramic Na₄.₉FeP₀.₁Si₃.₉O₁₂ [Fig. 4(c)], respectively.

### 3.3 Ionic conduction properties of glass-ceramics

Figures 5(a)–5(c) show the observed complex impedance diagrams for the representative glass-ceramic specimens of the mother Na₅FeSi₄O₁₂, the more conductive Na₅.₂FeB₀.₂Si₃.₈O₁₂ and Na₄.₉FeP₀.₁Si₃.₉O₁₂, which were analyzed according to the universal equivalent circuit. As can be seen in the figure, the complex impedances were comprised of 1 semi-circle at the temperatures of lower than 200 °C and higher than 300 °C on all the specimens. The intercepting points on the real axis were considered as the total impedances of the whole glass-ceramics (R_T), and the calculated impedances are summarized in Table 3. The enhancement of conductivity was attained with both compositional systems of Na₅₊ₓFeBₓSi₄₋ₓO₁₂ and Na₅₋ₚFePₚSi₄₋ₚO₁₂ within solubility limits of x < 0.4 and y < 0.3, and the respective highest total conductivities of σₗ were improved from 1.₃ × 10⁻³ up to 3.₁ × 10⁻³ for Na₅.₂FeB₀.₂Si₃.₈O₁₂ and 4.₂ × 10⁻³ S cm⁻¹ at 300 °C [σₗ (300)] for Na₄.₉FeP₀.₁Si₃.₉O₁₂, respectively (Table 3). The calculated results of the three specimens are compared in the Arrhenius plots (Fig. 6), where the activation energies for the whole conduction for the three were calculated as 52.₁, 50.₅, and 42.₁ kJ mol⁻¹, respectively. The value of Na₄.₉FeP₀.₁Si₃.₉O₁₂ was somehow smaller than the other two.

It was also noted that the impedance diagrams consisted of 2 intercepting points on the real axes at medium temperatures of 250 and 300 °C [Figs. 5(a)–5(c)], which were assigned to the contribution of grains (R_G) and grainboundaries (R_GB) according to the universal analyses. The values of R_T were therefore expressed as R_T = R_G + R_GB. Despite the limited numbers of data, Table 3 also includes the calculated conductivities of grains (σ_G) and grainboundaries (σ_GB) measured at 250 °C and 300 °C. The same ratios of thickness to surface area were conveniently used for the calculation of both σ_G and σ_GB, since the shapes of some grainboundaries were undefinable. Table 3 also contains the calculated ratios of measured R_GB/R_T. The dependence of the ratios on temperature indicates that the conduction through grainboundaries can dominate the total conduction at lower temperatures, while the whole conduction can be predominated by the conduction intra grains at higher temperatures.

The effects of substituting elements are summarized as the compositional dependence of σₗ on the values of x and y (Fig. 7). As seen from the figure, the substitution of Si with B and P were effective and the maximum conductivities of σₗ (300) and σₗ (250) were realized with the substitution x = 0.₂ and y = 0.₁ for Na₅₋ₓFeBₓSi₄₋ₓO₁₂ and Na₅₋ₚFePₚSi₄₋ₚO₁₂, as σₗ (300) as 3.₁ × 10⁻³ and 4.₂ × 10⁻³ S cm⁻¹ with Ea_T of 50.₅ and 42.₁ kJ mol⁻¹, respectively.

The effect of Si substitution on the total conduction was more effectively with P than B (Fig. 7). The effect of B substitution can be explained with shrinkage in the size of 12-membered tetrahedral rings, giving expansion of paths for sodium ions to conduct among those rings (see Fig. 1 with Table 2). In addition to the lattice shrinkage, the P substitution can also be attributable to the increase of sodium ion vacancies ([V_Na⁺]) for conduction because [V_Na⁺] increased proportionally with the concentration of P as.
Table 3. Conduction properties of Na₅FeSi₄O₁₂, Na₅₃FeB₀₂Si₃₈O₁₂, and Na₄₉FeP₀₁Si₃₉O₁₂ glass-ceramics.

| °C  | σᵣ / S cm⁻¹ | σₑ / S cm⁻¹ | Rₑₐₑ / Rᵣ | σₑ / S cm⁻¹ | Rₑₐₑ / Rᵣ | σₑ / S cm⁻¹ | Rₑₐₑ / Rᵣ | σₑ / S cm⁻¹ | Rₑₐₑ / Rᵣ |
|-----|--------------|--------------|-------------|--------------|-------------|--------------|-------------|--------------|-------------|
| R.T. | 1.3 x 10⁻⁷   | —            | —           | 3.2 x 10⁻³   | —           | —            | —           | —            | —           |
| 50  | 5.0 x 10⁻⁷   | —            | —           | 1.4 x 10⁻⁶   | —           | —            | —           | —            | —           |
| 100 | 5.8 x 10⁻⁶   | —            | —           | 1.5 x 10⁻⁵   | —           | —            | —           | —            | —           |
| 150 | 3.7 x 10⁻⁵   | —            | —           | 9.4 x 10⁻⁴   | —           | —            | —           | —            | —           |
| 200 | 1.6 x 10⁻⁴   | —            | —           | 3.5 x 10⁻³   | —           | —            | —           | —            | —           |
| 250 | 5.1 x 10⁻⁵   | 1.1 x 10⁻³   | 9.6 x 10⁻⁴ | 2.2 x 10⁻⁴   | 2.6 x 10⁻³  | 4.6          | 7.9 x 10⁻⁴  | —            | —           |
| 300 | 1.3 x 10⁻³   | 1.5 x 10⁻³   | 1.1 x 10⁻² | 3.1 x 10⁻⁴   | 3.5 x 10⁻³  | 6.0 x 10⁻⁴   | 7.9 x 10⁻⁴  | —            | —           |
| 350 | 2.9 x 10⁻³   | —            | —           | 6.0 x 10⁻⁴   | —           | —            | —           | —            | —           |
| 400 | 1.2 x 10⁻²   | —            | —           | 2.2 x 10⁻³   | —           | —            | —           | —            | —           |

Eₐ/kJ mol⁻¹ = 52.1

Fig. 6. Arrhenius plots for Na₅FeSi₄O₁₂, Na₅₃FeB₀₂Si₃₈O₁₂, and Na₄₉FeP₀₁Si₃₉O₁₂ glass-ceramics.

Fig. 7. Effects of Si-substituting element on ionic conductivities of Na₅FeSi₄O₁₂, Na₅₃FeB₀₂Si₃₈O₁₂ (x = 0.1–0.3), and Na₄₉FeP₀₁Si₃₉O₁₂ (y = 0.1, 0.2) glass-ceramics at room temperature and 300 °C.

Table 4. Total conductivities and electronic conductivities and the Na⁺ transference numbers of Na₅FeSi₄O₁₂, Na₅₃FeB₀₂Si₃₈O₁₂ (x = 0.1–0.3), and Na₄₉FeP₀₁Si₃₉O₁₂ (y = 0.1, 0.2) glass-ceramics.

|         | σᵣ / x 10⁻² S cm⁻¹ | σₑ / x 10⁻¹ S cm⁻¹ | t⁺ |
|---------|---------------------|---------------------|----|
| Na₅FeSi₄O₁₂ | 1.33                | 1.18               | 0.991 |
| Na₅₃FeB₀₂Si₃₈O₁₂ | 1.69              | 1.21               | 0.993 |
| Na₄₉FeP₀₁Si₃₉O₁₂ | 3.05              | 1.30               | 0.996 |
| Na₅FeSi₄O₁₂ | 2.27                | 2.01               | 0.989 |
| Na₅₃FeB₀₂Si₃₈O₁₂ | 4.21              | 1.63               | 0.996 |
| Na₄₉FeP₀₁Si₃₉O₁₂ | 2.79               | 1.12               | 0.996 |

σᵣ: Total conductivity.
σₑ: Electronic conductivity.
t⁺: Na⁺ transference number.

[Vₐₙa] = 5 – (5 – y) = y, and y = 0.1 was the optimum concentration (Fig. 7). In the case of B substitution, the vacancies were partially occupied with the excess sodium ions (|CexNa|) as |CexNa| = (5 + x) – 5 = x.

Also mentioned above is the possible predominance of σᵣ by the properties of grainboundaries at lower temperatures. Because of the less conductivity, the number of grainboundaries was attributable to the total conductivity. SEM observation exhibited the fewer number of grain-boundaries in Na₄₉FeP₀₁Si₃₉O₁₂ than Na₅FeSi₄O₁₂ and
Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$ [Figs. 4(a)–4(c)]. Control of the microstructure of grain-size can be reasonably thought to be important for applications at lower temperatures such as all-solid-state batteries.

The V–I relationship measured on Na$_{4.9}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$ by Wagner polarization method is shown as an example to evaluate Na$^+$ ion transference numbers ($t_i$) (Fig. 8). All the glass-ceramic specimens showed satisfactory results of $t_i$ being nearly 1 (Table 4), indicating pure sodium ionic conduction in those glass-ceramics.

4. Conclusions

We successfully improved the sodium ion conductivity of rare earth-free Na$_5$FeSi$_4$O$_{12}$ glass-ceramics using the compositions of Na$_{5.1}$xFeB$_x$Si$_{4-1}$xO$_{12}$ and Na$_{4.9}$xFeP$_y$Si$_{4-1}$yO$_{12}$. The attained conductivities were enhanced from 1.3 x 10$^{-3}$ to 3.1 x 10$^{-3}$ and 4.2 x 10$^{-3}$ S cm$^{-1}$ at 300 °C for Na$_{5.2}$FeB$_{0.2}$Si$_{3.8}$O$_{12}$ and Na$_{4.9}$FeP$_{0.1}$Si$_{3.9}$O$_{12}$, respectively.

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