Development of Na+ superionic conducting Na₅YSi₄O₁₂-type glass-ceramics

Toshinori Okura*

Department of Applied Chemistry, School of Advanced Engineering, Kogakuin University, 2665-1 Nakano, Hachioji-shi, Tokyo 192-0015, Japan

*Corresponding author: Tel: (+81) 426284149; E-mail: okura@cc.kogakuin.ac.jp

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Abstract

This review article describes a series of studies on the glass-ceramic Na+ superionic conductors with Na₅YSi₄O₁₂ (N5)-type structure synthesized using the composition formula of Na₃₋ₓ₋₉ₓ₋₉₋ₓ₋₇₋ₓ₋₉₋₉₋ₓ₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉₋₉-...
the Na2O-Y2O3-P2O5-SiO2 system [10]. These N5-type materials have been obtained, as well as N3-type [11-13] materials, with the composition formula originally derived for N3-type solid solutions and expressed as follows [14].

$$\text{Na}_{3x+2y} \text{Y}_{1-x} \text{P}_2 \text{Si}_{3+y} \text{O}_9 (x \geq 0.6, y \leq 0.5) \quad (1)$$

With the aim of searching for more conductive glass-ceramic N5-type materials, the verification of the validity of the generalized composition formula

$$\text{Na}_{3x+2y} \text{R}_1 \text{P}_2 \text{Si}_{3+y} \text{O}_9 (R = \text{rare earth ions}) \quad (2)$$

for the synthesis of other kinds of rare earth N5-type glass-ceramics was studied. For convenience, the present materials are abbreviated as NaRPSi taken from the initials of the Na2O-R2O3-P2O5-SiO2 system.

In this review, the optimum conditions for crystallization were discussed with reference to the conduction properties and the preparation of crack free N5-type glass-ceramics. The effects of Si substitution with the various elements with tetrahedral oxygen coordination structure and Y substitution with the various R elements were also discussed on ionic conductivity of N5-type glass-ceramics, respectively.

**Preparation of crack free NaYPSi4O12-type glass-ceramics containing the largest Sm2+ ions: crystallization condition and ionic conductivity [15-17]**

Glass-ceramics of the phosphorus containing N5-type [5, 6] Na⁺ superionic conductors [10, 18] have been developed by crystallization of glasses with the composition formula 2 [14, 19, 20]. The R elements have a significant effect on the crystallization of glasses [19], as well as on the conduction properties [5]. To date, polycrystalline N5-type NaRPSi has been obtained with Sc, Y, Gd or Sm as the R element. The ionic radius of R (sixfold oxygen coordinated R) has been expected to have a significant effect on the crystallization of the phase. The reported results on the silicate ceramics [5] show that the conductivity of the N5-type NaRPSi increases with increasing ionic radius of R, giving the order NaSmPSi > NaGdPSi > NaYPSi > NaScPSi. It can be expected that NaSmPSi is the most conductive [21]. However, this order was not always true in glass-ceramics [22]. Although most of the NaRPSi compounds were obtained as crack free bulky glass-ceramics (15 mm in diameter, 5 mm in thickness), NaSmPSi was difficult to prevent from cracking during crystallization. It was found that crack free NaGdPSi with larger Gd³⁺ ions was the most conductive; however, NaSmPSi with the largest Sm³⁺ ions was less conductive than NaYPSi with medium Y²⁺ ions. In the present study, the N5-type NaSmPSi ionic conductors were prepared by crystallization of glasses. The optimum conditions for crystallization were discussed with reference to the conduction properties and the preparation of crack free N5-type glass-ceramic NaSmPSi.

Samples were prepared according to the chemical formula mentioned above of Na3x+2ySm1-xP3Si3+yO9. The temperatures employed for nucleation and crystallization of glass specimens were also determined by the results of DTA analysis. Fig. 2 shows the program of temperature and time for the production of glass-ceramic NaSmPSi employed in the present work. The N5-type NaSmPSi ionic conductors were successfully produced by crystallization of glasses. Although the glass samples heated by the program pattern (A) shown in Fig. 2 broke during crystallization and the glass-ceramic NaSmPSi obtained by the pattern (B) was difficult to prevent from cracking during crystallization, most of the NaSmPSi compounds by the pattern (C) were obtained as crack free bulky glass-ceramics (the glass samples broke during crystallization when heating time for crystallization was over 5 h).

Fig. 2. Program of temperature and time for the production of NaSmPSi glass-ceramics.

Fig. 3. The diagram of phase-composition of NaSmPSi glass-ceramics crystallized at 900°C.

**Fig. 3** shows the phase-composition diagram of samples crystallized at 900 °C by the pattern (C). The crystallization of the N5 single-phase glass-ceramic NaSmPSi was dependent strongly on the concentrations of both [R] and [P] (or x and y in the composition parameters) and the temperature for crystallization of
glass specimens. Fig. 4 shows SEM photograph of microstructure of specimen with the Na$_3$Smo$_{0.3}$P$_{0.3}$Si$_{1.2}$O$_9$ composition heated at 900 °C by the pattern (c). The grain size of the specimen was about 3-5 μm. The state of grain growth is promoted with increase of heating temperature and heating time for crystallization. Although grain growth may cause high conductivity, it was difficult to prevent the sample heated for a long time from cracking during crystallization. Studies are underway to produce a crack free sample. Conduction properties were measured by the ac two-probe method on cylindrical glass-ceramics of typically 15 mm in diameter and 2 mm in thickness with an LF impedance analyzer. Electrodes were prepared by sputtering of gold on polished surfaces. The applied ac field ranged from 5 to 10 MHz in frequency. The temperature dependence of the conductivity was measured in a similar way at several temperatures ranging from room temperature to 350 °C. Table 1 summarizes the conduction properties of the N5-type glass-ceramic NaSmPSi specimens. It was found that NaSmPSi containing the largest Sm$^{3+}$ ions was less conductive than NaYPSi with medium Y$^{3+}$ ions as the grain sizes of the presented specimens were very small.

Table 1. Conduction properties of N5-type NaSmPSi glass-ceramics. Heat-treatment: 900 °C, 5 h.

<table>
<thead>
<tr>
<th>Mix proportion</th>
<th>$\sigma_{300}$ / 10$^{-1}$ S cm$^{-1}$</th>
<th>$E_a$ / kJ mol$^{-1}$</th>
<th>T</th>
<th>G</th>
<th>G. B.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ $y$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>0.30</td>
<td>0.238</td>
<td>27.6</td>
<td>17.9</td>
<td>51.4</td>
</tr>
<tr>
<td>0.45</td>
<td>0.40</td>
<td>0.408</td>
<td>30.4</td>
<td>18.8</td>
<td>95.7</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35</td>
<td>0.352</td>
<td>19.5</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.40</td>
<td>0.478</td>
<td>29.3</td>
<td>16.6</td>
<td></td>
</tr>
</tbody>
</table>

$\sigma_{300}$: conductivity at 300°C

$E_a$: activation energy (T: total, G: grain, G. B.: grain boundary)

Effect of substitution of Si with Ge and Te on ionic conductivity of Na$_3$YSi$_{12}$-type glass-ceramics [23]

Our phosphorus containing compositions have been confirmed superior to the mother composition of NaRSi$_{12}$, especially in the production of the single-phase glass-ceramics. Considering the inference, our main work has recently been focused on the synthesis of various glass-ceramics with single-phase Na$_3$RSi$_{12}$. In the present study, the N5-type glass-ceramics of the germanium- or tellurium-containing Na$^+$ superionic conductors (NaSmXSi) from the glasses with the composition Na$_{3+x}$Sm$_{1-x}$O$_{y}$Si$_{12}$O$_9$ (X=Ge; NaSmGeSi, X=Te; NaSmTeSi) were prepared, and the effects of X elements on the separation of the phase and the microstructural effects on the conduction properties of glass-ceramics were discussed.

The glass-ceramics have been obtained under the appropriate sets of the parameters $x$ and $y$ of the composition formula Na$_{3+y}$Sm$_{1-x}$O$_{y}$Si$_{12}$O$_9$ ranging in $x = 0.3 - 0.55$ and $y = 0.2 - 0.45$. The precursor glasses were made by melting stoichiometric mixtures of reagent-grade powders of anhydrous Na$_2$CO$_3$, Sm$_2$O$_3$, GeO$_2$, TeO$_2$ and SiO$_2$ at 1300-1400°C for 1 h, followed by annealing for several hours at an optimum temperature. The N5-type NaSmXSi ionic conductors were successfully produced by crystallization of glasses. Fig. 5 shows the diagrams of phase-composition of NaSmGeSi (a) and NaSmTeSi (b) glass-ceramics. The N5-type NaSmXSi is obtained as a stable phases at high-temperatures. The crystallization of N5 single phase is strongly dependent both on the contents of samarium and (germanium or tellurium) ions (or the values $x$ and $y$ correspond to the composition parameters in Na$_{3+y}$Sm$_{1-x}$O$_{y}$Si$_{12}$O$_9$). N3 and N9 phases can be crystallized as the high-temperature stable phases at the regions of higher [Sm] and rather lower [Sm], respectively. The combination of $x$ and $y$ was most varied in N5-type NaSmPSi and more limited in the order N5-type NaSmGeSi>N5-type NaSmTeSi. Table 2 summarizes the conduction properties of the N5-type glass-ceramic NaSmPSi and NaSmXSi with the Na$_{3+y}$Sm$_{0.3}$P$_{0.3}$Si$_{1.2}$O$_9$ and Na$_{3+y}$Sm$_{0.6}$X$_{0.2}$Si$_{1.2}$O$_9$ compositions, respectively. Their conductivities and activation energies are of the order of 10$^{-2}$ S/cm at 300°C and of 19 to 23 kJ/mol, respectively. The conductivity of these samples decreases with the increase of the bond length (P-O: 0.156 nm, P=O: 0.150 nm, Ge-O: 0.187 nm, Te-O: 0.208 nm), giving the order NaSmPSi>NaSmGeSi>NaSmTeSi.

![Fig. 4. SEM photograph of the specimen with Na$_{3+y}$Sm$_{0.3}$P$_{0.3}$Si$_{1.2}$O$_9$ composition heated at 900 °C by the pattern (c).](image)

![Fig. 5. The diagrams of phase-composition of NaSmGeSi (a) and NaSmTeSi (b) glass-ceramics crystallized at 950°C.](image)
Table 2. Conduction properties of N5-type NaSmPSi and NaSmXSi glass-ceramics.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heat-treatment</th>
<th>( \sigma_{300} ) /10(^4) S·cm(^{-1})</th>
<th>( E_a ) /kJ·mol(^{-1})</th>
<th>T</th>
<th>G</th>
<th>G. B.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSmPSi</td>
<td>900</td>
<td>0.66</td>
<td>22.8</td>
<td>14.4</td>
<td>44.7</td>
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<tr>
<td></td>
<td>900</td>
<td>0.38</td>
<td>19.2</td>
<td>18.4</td>
<td>59.8</td>
<td></td>
</tr>
<tr>
<td>NaSmGeSi</td>
<td>950</td>
<td>0.48</td>
<td>20.4</td>
<td>19.2</td>
<td>69.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.54</td>
<td>23.8</td>
<td>21.7</td>
<td>70.7</td>
<td></td>
</tr>
<tr>
<td>NaSmTeSi</td>
<td>850</td>
<td>0.28</td>
<td>20.8</td>
<td>19.9</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>0.36</td>
<td>21.3</td>
<td>20.8</td>
<td>44.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>0.43</td>
<td>22.6</td>
<td>21.4</td>
<td>50.7</td>
<td></td>
</tr>
</tbody>
</table>

\( \sigma_{300} \): conductivity at 300°C  
\( E_a \): activation energy (T: total G: grain G. B.: grain boundary)

\( \text{Na}^+ \) superionic conductors of Na\(_3\)YSi\(_2\)O\(_{12}\)-type glass-ceramics in the system Na\(_2\)O-Sm\(_2\)O\(_3\)-X\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\) (X=Al, Ga) [24]

The N5-type glass-ceramics of the aluminum or gallium, and phosphorus-containing Na\(^+\) superionic conductors (NaSmXPSi) from the glasses with the composition Na\(_{3+3x-y}\)Sm\(_x\)-X\(_3\)-P\(_3\)O\(_9\) (X = Al; NaSmAlPSi, X = Ga; NaSmGaPSi) were prepared, and effects of X elements on the separation of the phase and the microstructural effects on the conduction properties of glass-ceramics were discussed.

Glass-ceramic NaSmXPSi specimens were prepared with the parameters \( x = 0.4, y = 0.3 \) and \( z = 0.1-0.4 \). The precursor glasses were made by melting stoichiometric mixtures of reagent-grade powders of anhydrous Na\(_2\)CO\(_3\), Sm\(_2\)O\(_3\), X\(_2\)O\(_3\), NH\(_4\)H\(_2\)PO\(_4\) and SiO\(_2\) at 1350 °C for 1 h, followed by annealing at a temperature of 500 °C to 600 °C for several hours, depending on the kind and concentration of X. The annealed specimens were heated up to 600°C to 1000°C for 5 h for crystallization. The N5-type NaSmXPSi ionic conductors were successively produced by crystallization of glasses with the parameter \( z = 0.1 \). The effect of composition on the temperature at which N5-type NaSmXPSi is transformed from the precursor N9-type NaSmXPSi may be recognized in the phase-temperature maps illustrated in Fig. 6. The N5-type NaSmXPSi was obtained as a stable phase at high-temperatures. The crystallization of N5 single phase NaSmXPSi is strongly dependent on the content of aluminum or gallium ion (or the value z). N9 phase can be crystallized as the stable phases at the region of higher [X]. Table 3 summarizes the conduction properties of N5-type glass-ceramic NaSmXPSi. NaSmAlPSi and NaSmGaPSi showed the ionic conductivities of \( 0.67 \times 10^{-4} \) and \( 0.76 \times 10^{-4} \) S/cm at 300 °C, respectively. The ionic conductivity of glass-ceramic NaSmPSi was \( 0.24 \times 10^{-4} \) S/cm at 300 °C. It was found that NaSmXPSi was more conductive than NaSmPSi.

Fig. 6. Phase changes of glass-ceramics with temperature.  
(a) Na\(_3\)O-Sm\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\)  
(b) Na\(_3\)O-Sm\(_2\)O\(_3\)-Ga\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\)  
Phase notation: Na\(_3\)YSi\(_2\)O\(_{12}\)-type: N5, Na\(_3\)YSi\(_2\)O\(_{12}\)-type: N9

Table 3. Conduction properties of N5-type NaSmXPSi glass-ceramics (\( z = 0.1 \)). Heat-treatment: 1000°C, 5 h.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( \sigma_{300} ) / 10(^4) S·cm(^{-1})</th>
<th>( E_a ) /kJ·mol(^{-1})</th>
<th>T</th>
<th>G</th>
<th>G. B.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSmAlPSi</td>
<td>0.67</td>
<td>23.69</td>
<td>21.68</td>
<td>42.86</td>
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<tr>
<td>NaSmGaPSi</td>
<td>0.76</td>
<td>26.04</td>
<td>17.06</td>
<td>40.00</td>
<td></td>
</tr>
</tbody>
</table>

\( \sigma_{300} \): conductivity at 300°C  
\( E_a \): activation energy (T: total G: grain G. B.: grain boundary)

Synthesis and Na\(^+\) conduction properties of Nasicon-type glass-ceramics in the system Na\(_2\)O-Y\(_2\)O\(_3\)-R\(_2\)O\(_3\)-P\(_2\)O\(_5\)-SiO\(_2\) (R=rare earth) and effect of Y substitution [25]

Glass-ceramics of the phosphorus-containing N5-type Na\(^+\)-superionic conductors were prepared by crystallization of glasses with the composition Na\(_{3+3x-y}\)Y\(_{1-x}\)-R\(_x\)P\(_3\)Si\(_3\)O\(_9\) (NYPS; R=Nd, Sm, Eu, Gd, Dy, Er, Yb) \((x=0.4, y=0.2, z=0.1)\). In the present study, the various R elements were substituted for the yttrium. The crystallization kinetics of the glasses was examined by DTA, and the effects of R elements on the separation of the phase and the microstructural effects on the conduction properties of glass-ceramics were discussed.
Fig. 7. Lattice constants of NY(Nd, Sm, Eu, Gd, Dy, Er, Yb)PS and NYPS glass-ceramics.

Fig. 8. Activation energies ($E_a$) of crystal growth of NY (Nd, Sm, Eu, Gd, Dy, Er, Yb)PS and NYPS glasses.

The precursor glasses were made by melting stoichiometric mixtures of reagent-grade powders of anhydrous Na$_2$CO$_3$, Y$_2$O$_3$, R$_2$O$_3$ (R= Nd, Sm, Eu, Gd, Dy, Er, Yb), NH$_4$H$_2$PO$_4$ and SiO$_2$ at 1350°C for 1 h after calcinations at 400 °C for 0.5 h and 900 °C for 0.5 h. The N5-type glass-ceramic NYRPS and NYPS (Y-Narpsio) with the Na$_{4.4}$Y$_{0.6}$P$_{0.2}$Si$_{2.8}$O$_9$ composition, respectively, were successfully synthesized by crystallization of glasses. The lattice constant of the glass-ceramic NYRPS increases as the ionic radius of R is increased (Fig. 7). The formation of N5-type structure from the precursor glasses is a matter of crystallization kinetics. The substitution of large R ions has the weakening effect on the bonding of the N3- or N9-type skeleton structure of 6-membered SiO$_4$-tetrahedra rings, resulting in the tendency to form the stable N5-type 12-membered structure. The conductivity of the NYRPS glass-ceramics increases as the ionic radius of R is increased (Fig. 9). It is presumed that rare earth ions, octahedrally coordinated with the non-bridging oxide ions of the 12-membered rings of silica tetrahedra, work to expand the conduction paths for Na$^+$ ions along the c-axis [5], which can explain the observed dependence of activation energies on ionic radius of R in this work.

Fig. 9. Conductivity at 300°C of NY (Nd, Sm, Eu, Gd, Dy, Er, Yb)PS and NYPS glass-ceramics.

**Conclusion remarks**

In this review article, Na$^+$ superionic conducting glass-ceramics with N5-type structure were presented for a variety of rare earth elements R, using the sodium rare earth silicophosphate composition of Na$_{3+3x}$R$_{1-x}$P$_x$Si$_{3-y}$O$_9$. These glass-ceramic conductors have great potential, and is one of the most important groups of solid electrolytes, not only because it is practically useful for advanced batteries, but also because it is a three-dimensional ionic conductor, which comprises 12-(SiO$_4$)$_4$-tetrahedra membered skeleton structure, from which or by analogy with which various kinds of solid electrolyte materials can be derived. It is a solid solution in the Na$_2$O-R$_2$O$_3$-P$_2$O$_5$-SiO$_2$ system. A variety of modified Narpsios have been synthesized by replacing R with Y, Nd, Sm, Eu, Gd, Dy, Er, Yb, and/or by substituting tetra (Ge$^{4+}$, Te$^{4+}$) and tri (Al$^{3+}$, Ga$^{3+}$) valent ions for P or Si. The use of glass-making processing is favorable for the fabrication of various shaped electrolyte, and the microstructure of glass-ceramic electrolyte is possible to control by changing of crystallization condition.

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