CRYSTALLIZATION AND CONDUCTION PROPERTY OF Na⁺ SUPERIONIC CONDUCTOR NARPSIO-V

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ABSTRACT

Various Narpsios consisting of the composition formula of $\text{Na}_{3+3x-y}\text{R}_{1-x}\text{PySi}_{3-y}\text{O}_9$ (R : rare earth, In and Sc) were synthesized by the crystallization of a glass. The formation of Narpsio-V having high conduction property was influenced by the kind of R element. The specimens with single phase of Narpsio-V were obtained in the use of Sm, Eu, Gd, Y and Er. In particular, the Narpsio-V widely yielded on the composition map of [Y] vs. [P]. The R elements also affected the conduction properties. The activation energy for Na⁺ conduction in Narpsio-V was improved with increasing the ionic radius of R element. Although the lowest activation energy was confirmed in the case of Sm, the total conductivity of whole specimen with Sm was lower than that with Gd. This was due to the difference in the grain boundary.

INTRODUCTION

It was found Na⁺ superionic conductors (called Narpsio) with the composition formula of $\text{Na}_{3+3x-y}\text{R}_{1-x}\text{PySi}_{3-y}\text{O}_9$ in the system $\text{Na}_2\text{O-R}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ (R : rare earth elements)¹⁻⁷⁾. The Narpsio has three crystal structures analogizing with those of $\text{Na}_3\text{RSi}_3\text{O}_9$, $\text{Na}_5\text{RSi}_4\text{O}_{12}$ and $\text{Na}_9\text{RSi}_6\text{O}_{18}$. Those compounds in Narpsio were abbreviated as Narpsio-III, Narpsio-V and Narpsio-IX, respectively¹⁾. The ionic conductivity of Narpsio was strongly dependent upon the crystal structures and high conductivity was observed in Narpsio-V²⁾. To date, we have obtained the result that the Narpsio-V with Gd exhibits the total conductivity of 1.3×10^{-1} S/cm at 300 °C and the activation energy of 23 kJ/mol for Na⁺ conduction³⁾. As the R elements in Narpsio-V played an important role of binding 12-membered rings formed by SiO_4 and PO_4 tetrahedrons in the crystal structure¹⁾, the formation of

that was influenced by the kind of R element. In this paper, it is reported the composition map for the single phase of Narpsio-V with various R elements. We also show the relationship between the conduction properties and R elements.

EXPERIMENTAL

Various Narpsio glasses were prepared by melting at 1350 °C for 1 h in a platinum crucible the mixed reagent-grade powders of anhydrous Na_2CO_3 , R_2O_3 (R = Sc, In, Er, Y, Gd, Eu, Sm, Nd and La), $\text{NH}_4\text{H}_2\text{PO}_4$ and SiO_2 according to the above composition formula. For convenience, those will be referred to as R-Narpsio substituting the symbol of each rare-earth, In and Sc element for R. Narpsio with the composition of $\text{Na}_{3.9}\text{R}_{0.6}\text{P}_{0.3}\text{Si}_{2.7}\text{O}_9$ was adjusted in order to measure the conduction properties. The obtained glasses were treated at 500 °C for 1 h followed by crystallizing at temperature just below the melting points for 48 h, sufficient time for crystallization, except Sm- and Eu-Narpsio. As the bulky glasses of Sm- and Eu-Narpsio broke during the crystallization, these specimens were synthesized by sintering the compacted glass powders.

The conduction properties were determined by a complex admittance method for frequencies between 10 Hz and 10 MHz at 150 °C to 350 °C in air. The crystalline phase was identified by X-ray diffraction equipment using Cu target.

Figure 1 XRD patterns of Sm-, Gd-, In- and Nd-Narpsio.

RESULTS AND DISCUSSION

The powder XRD patterns of Narpsio with various R elements (In, Gd, Sm and Nd) are shown in Fig.1. The single phase of Narpsio-V was obtained by employing Y and Sm. The results for the specimens with Er, Gd and Eu were similar to those for Y-Narpsio. In-Narpsio as well as Sc-Narpsio consisted of the mixture phase of Narpsio-V and unknown phase. On the other hand, no peaks attributed to Narpsio-V, Narpsio-III and/or Narpsio-IX were confirmed in the specimens with Nd and La. The order of trivalent ionic radius of those elements are represented as giving below :

$$\text{Sc} < \text{In} < \text{Er} < \text{Y} < \text{Gd} < \text{Eu} < \text{Sm} < \text{Nd} < \text{La}.$$

From the above results, it becomes apparent that the elements with the ionic radius in the range of $1.02\text{\AA}$ to $1.104\text{\AA}$ are suitable for the formation of Narpsio-V.

Figure 2 The region where single Narpsio-V phase yielded on the composition map of [R] vs. [P].

Table 1 Conduction properties of various Narpsios

Composition	Ea / kJmol^{-1}	Total conductivity $\sigma_{300} / \text{Scm}^{-1}$	Crystal phase
Sc -Narpsio	35.3	3.2×10^{-3}	Narpsio-V+unknown
In -Narpsio	39.8	3.1×10^{-3}	Narpsio-V+unknown
Er -Narpsio	26.9	3.6×10^{-2}	Narpsio-V
Y -Narpsio	26.6	6.6×10^{-2}	Narpsio-V
Gd -Narpsio	23.0	1.3×10^{-1}	Narpsio-V
Eu -Narpsio	24.4	5.2×10^{-2}	Narpsio-V
Sm -Narpsio	20.9	6.3×10^{-2}	Narpsio-V
Nd -Narpsio	55.1	2.2×10^{-5}	non-Narpsio
La -Narpsio	57.8	1.6×10^{-4}	non-Narpsio

Figure 3 Relationship between the activation energy for Na^+ conduction in Narpsio-V and ionic radius of R element.

The regions where the single phase of Narpsio-V with Sm, Gd, Y and Er was obtained on the composition map [R] vs. [P] are shown in Fig.2. The crystallization of Narpsio-V was strongly dependent on the kind of R element. The Y-Narpsio yielded on the wide composition compared to Narpsio-V with other elements. This indicates that the Y is more useful element for the preparation of specimen with single Narpsio-V phase. From the results in Fig.1 and Fig.2, it is further suggested that Y has the optimum ionic radius as the atoms binding 12-membered rings consisted of SiO₄ and PO₄ tetrahedrons in Narpsio-V structure.

The conduction properties of various Narpsios are summarized in Table1. The Sm-, Eu-, Gd-, Y- and Er-Narpsio with the single Narpsio-V phase exhibited high conductivity, whereas the conduction properties of the specimens without Narpsio-V (in case of La and Nd) and with the unknown phase (in case of In and Sc) were poor. The most conductive Narpsio was Gd-Narpsio.

Figure 3 shows the relationship between the ionic radius of R elements and the activation energy for Na⁺ conduction in each grain. The activation energy decreased with increasing the ionic radius up to 1.104Å and rapidly increased above that. It is considered that the high activation energy in Nd- and La-Narpsio relates to the appearance of different phase from Narpsio-V. This result indicates that larger R elements are favorable for the Na⁺ conduction. That is, it is suggested that Na⁺ conduction path in Narpsio-V is extended with the size of R element. The lowest activation energy was observed in the Sm-Narpsio. The Sm-Narpsio, however, showed the low conductivity compared to Gd-Narpsio. The large grain boundary resistance was observed in the Sm- and Eu-Narpsio synthesized by sintering the compacted disk consisting of the glass powders. On the contrary, the remarkable influence of grain boundary on the conductivity was hardly confirmed in specimens such Gd- and Y-Narpsio prepared from bulky glass. Those facts demonstrate that the lower conductivity in the Sm- and Eu-Narpsio results from the large resistance at grain boundary. If the Sm-Narpsio had been successfully prepared from the crystallization of bulky glass, that would have showed the higher conductivity.

CONCLUSION

We have studied the influence of ionic radius of R element in Narpsio on the conduction properties and formation of Narpsio-V with high Na⁺ conduction. Here, it was proved the signification of R element in Narpsio. The Narpsio-V was formed with the R elements ranging in ionic radius from 1.02Å to 1.104Å. Employing Y, the region where the single phase of Narpsio-V was observed was remarkably expanded on the composition map of [R] vs. [P]. The activation energy for Na⁺ conduction decreased with increasing the ionic radius of R element, giving the expanse of conduction path for Na⁺. The Sm-Narpsio had the lowest activation energy. The total conductivity of whole specimen with smaller Gd, however, was higher than that with larger Sm. This was attributable to the high resistance at

grain boundary in the Sm-Narpsio.

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