Development of Narpsio solid electrolytes with Na^+-superionic conductivity prepared by crystallization of glasses

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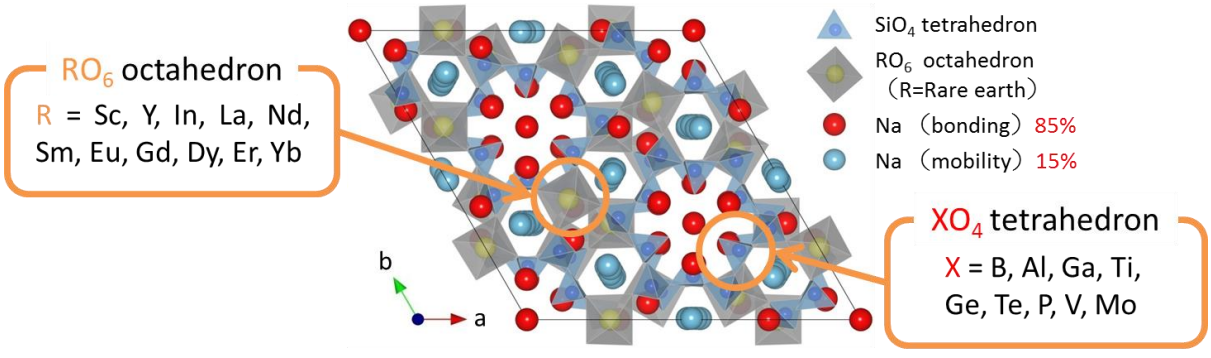
Abstract

This paper describes a series of studies on the Na^+ superionic conducting glass-ceramics with $Na_5YSi_4O_{12}$ (N5)-type structure synthesized using the composition formula of $Na_{3+3x-y}R_{1-x}P_ySi_{3-y}O_9$ for a variety of rare earth elements, R, under the appropriate composition parameters (Narpsio) [1]. The possible combinations of *x* and *y* became more limited for the crystallization of the superionic conducting phase as the ionic radius of R increased, while the Na^+ conduction properties were more enhanced in the glass-ceramics of larger R. The meaning of the composition formula can be signified in the thermodynamic and kinetic study of crystallization and phase transformation of metastable to stable phase in the production of N5-type glass-ceramics. It was demonstrated that the medium value of content product as [P]×[R] is important in the crystallization of N5 single phase. Conduction properties of these glass-ceramics were strongly dependent upon the crystallization conditions as well as compositions. Not only complex impedance analysis but also TEM observation confirmed that this dependence was attributed to the conduction properties of grain boundaries which were glasses condensed at triple points enclosed by grains.

The Narpsio family has 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_2O-R_2O_3-P_2O_5-SiO_2 system. A variety of modified Narpsios have been synthesized by replacing R with Sc, Y, In, La, Nd, Sm, Eu, Gd, Dy, Er, Yb, and/or by substituting tetra (Ti^{4+}, Ge^{4+}, Te^{4+}), tri (B^{3+}, Al^{3+}, Ga^{3+}), penta (V^{5+}), and hexa (Mo^{6+}) valent ions for P or Si [2].

Keywords: Narpsio, Solid electrolyte, Ionic conductivity, Glass-ceramics, Crystallization



Crystal structure of $Na_5RSi_4O_{12}$-type (R=rare earth) solid electrolyte.

References

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2. Okura, T.; Yoshida, N.; Yamashita, K. *Solid State Ionics* (Review) 2016, *285*, 143-154.