NOVEL CALCIUM ION CONDUCTING SOLID ELECTROLYTE WITH NASICON-TYPE STRUCTURE

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Key Words: Calcium ion, Solid Electrolyte, NASICON-type Structure

Divalent calcium ion conducting solid electrolyte with a three dimensional NASICON-type structure, $(Ca_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$[1], was successfully prepared by introducing Ca^{2+} cations into the $HfNb(PO_4)_3$ solid. The existence of three kinds of high valence cation of Hf^{4+}, Nb^{5+}, and P^{5+} successfully realized the effective reduction of electrostatic interaction toward Ca^{2+} in the structure. The $(Ca_{0.05}Hf_{0.95})_{4/3.9}Nb(PO_4)_3$ solid possesses considerably higher Ca^{2+} cation conductivity and also lower activation energy compared with those of previously reported NASICON-type $Ca_{0.5}Zr_2(PO_4)_3$[2] solid.

Figure 1 shows the compositional dependence of the lattice volume of the NASICON-type phase estimated by the lattice parameters. By doping Ca^{2+} ions into the Hf site in the structure, the lattice volume of the NASICON-type phase monotonously increased with x up to 0.05 due to the larger ionic size of Ca^{2+} (ionic radius: 0.114 nm)[3] compared with that of Hf^{4+} (ionic radius: 0.085 nm)[3], whereas those for the solids with $x \geq 0.05$ were kept almost constant. These results clearly suggest that the solid solubility limit of the single phase of NASICON-type $(Ca_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ is approximately $x = 0.05$. On the other hand, the conductivity monotonously enhanced with the Ca content until the solid solution limit of $x = 0.05$ (See Fig. 1).

Figure 2 presents the temperature dependence of the Ca^{2+} ion conductivity for $(Ca_{0.05}Hf_{0.95})_{4/3.9}Nb(PO_4)_3$ with the corresponding data for the NASICON-type $Ca_{0.5}Zr_2(PO_4)_3$[2]. The conductivity of the $(Ca_{0.05}Hf_{0.95})_{4/3.9}Nb(PO_4)_3$ solid was appreciably higher than that of the $Ca_{0.5}Zr_2(PO_4)_3$[2] solid in the temperature range measured.

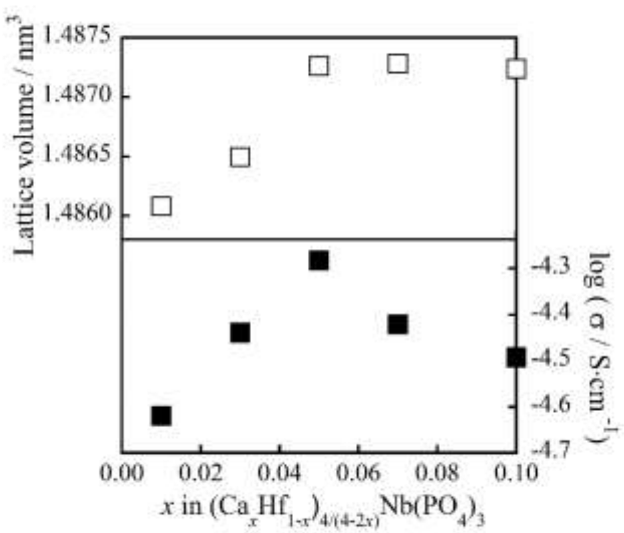

Figure 1 – Compositional dependencies of the lattice volume (□) and the ac conductivity (■) at 600 °C in air for $(Ca_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ (x = 0.01-0.10).

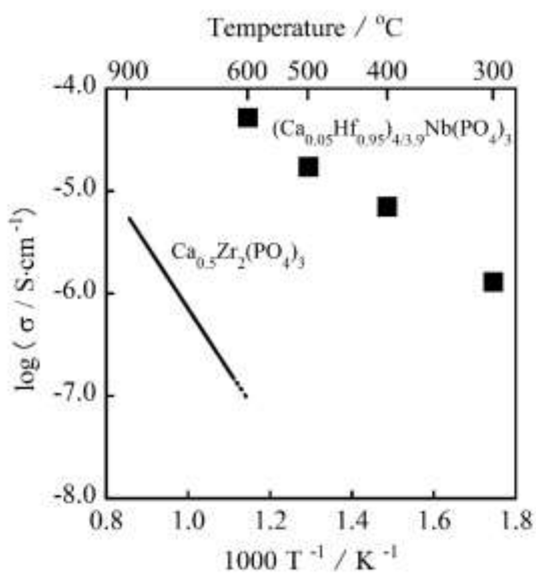

Figure 2 – The temperature dependencies on the ionic conductivity for $(Ca_{0.05}Hf_{0.95})_{4/3.9}Nb(PO_4)_3$ (■) and $Ca_{0.5}Zr_2(PO_4)_3$ (—).

References

1. Wonrak Lee, Shinji Tamura, and Nobuhito Imanaka, Chem. Lett., 2017, 46, 1487.
2. K. Nomura, S. Ikeda, and K. Ito, Bull. Chem. Soc. Jpn., 1992, 65, 3221.
3. R.D. Shannon, Acta Crystallogr., 1976, A32, 751