—Communication—

Sodium Ion Conductivity in the System

$\text{Na}_{1.5}(\text{A}_{2-y}, \text{B}_y)\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$; A, B: Zr, Ti, Hf

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1 INTRODUCTION

NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) fast ionic conductors have been extensively studied because of their structural interest since the discovery of Hong et al.¹⁾ The structure consists of a rigid three-dimensional network formed by PO_4/SiO_4 tetrahedra sharing corners with ZrO_6 octahedra and Na^+ ions located at interstitial sites of the network. A bottleneck in the sodium ion conduction path is a puckered hexagonal ring having sides that alternate between PO_4/SiO_4 tetrahedral and ZrO_6 octahedral edges.

Conductivity of NASICON is dominated by the concentration and mobility of the mobile ion. The latter is related to the size of the bottleneck. Partial substitutions of di-²⁻⁵⁾ or tri-^{6,7)} valent cations for Zr^{4+} ion have been investigated to enhance the total conductivity by increasing mobile ion concentration.

Substitution of a homovalent cation in the framework does not affect the Na^+ ion stoichiometry and therefore influences only the chemical and geometric factors in mobile ion transport. Cava et al.⁸⁾ have reported the conductivity changes by

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tetravalent cation substitution for Zr^{4+} ion. For all except the Hf^{4+} ion substitution, the conductivity decreased compared with that of NASICON at all measured temperatures. Wang et al.⁹⁾ investigated the ionic conductivity in the system of $\text{Na}_{1+x}\text{Hf}_{2-y}\text{Ti}_y\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($x=1.5$ and $x=2$) and concluded that the geometrical constraint plays an important role in determining the ion mobility.

$\text{Na}_{1.5}\text{A}_{2-y}\text{B}_y\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$ (A, B: Zr, Ti or Hf, $0 \leq y \leq 2$) were prepared to study the effect of bottleneck size on the conductivity while Na^+ ion content is kept constant. Systematic conductivity investigation has been attempted by comparing three kinds of systems.

2 EXPERIMENTAL

Three kinds of solid solutions, $\text{Na}_{1.5}(\text{A}_{2-y}\text{B}_y)\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$, where A and B were one of the tetra-valent ions, Zr^{4+} , Hf^{4+} and Ti^{4+} were prepared by a solid state reaction at 1150 or 1200°C for 10 h. Starting materials used were commercially obtained Na_2CO_3 , ZrO_2 , HfO_2 , TiO_2 (anatase), SiO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$. X-ray powder diffraction patterns of every sample were obtained using Rigaku RU-200B to identify the NASICON phase and to determine cell parameters by a least-square method. The sample powder was pressed into a pellet of 10mm in diameter in an evacuative die at 250 MPa and sintered at 1000°C for 3 h. Both sides of the pellet were coated with gold paint and heated at 600°C to evaporate solvent. Electrical conductivities were measured by a complex impedance

analysis at frequencies between 10Hz and 300kHz at temperatures between room temperature and 400°C using a Hewlett Packard 4800A vector impedancemeter.

3 RESULTS AND DISCUSSION

Figure 1 shows cell volumes as a function of composition y by use of the hexagonal a - and c -parameters. In both the systems $\text{Na}_{1.5}(\text{Zr}_{2-y}\text{Ti}_y)\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$ (abbreviated as $\text{Zr}_{2-y}\text{Ti}_y$) and $\text{Na}_{1.5}(\text{Hf}_{2-y}\text{Ti}_y)\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$ (abbreviated as $\text{Hf}_{2-y}\text{Ti}_y$), the cell volumes decreased with the increase of Ti^{4+} ion substitution. Dependence of cell volumes on y was very similar in both cases. This could be attributed to the similar ionic radii of Zr^{4+} ion (0.72Å) and Hf^{4+} ion (0.71Å) and to the smaller radius of Ti^{4+} ion (0.605Å)¹⁰. This idea can be applied to the cell volume change of the $\text{Zr}_{2-y}\text{Hf}_y$ system in which a smaller change was observed in comparison with those of $\text{Zr}_{2-y}\text{Ti}_y$ and $\text{Hf}_{2-y}\text{Ti}_y$ systems. These results suggest that the size of the bottleneck largely depends on the ionic size at the octahedral sites which forms the hexagonal puckered ring.

Fig.1. Variation of cell volume (V) versus composition (y) in the ○: $\text{Zr}_{2-y}\text{Ti}_y$, ●: $\text{Hf}_{2-y}\text{Ti}_y$ and □: $\text{Zr}_{2-y}\text{Hf}_y$ systems.

Conductivities at 300°C of $\text{Zr}_{2-y}\text{Ti}_y$, $\text{Hf}_{2-y}\text{Ti}_y$ and $\text{Zr}_{2-y}\text{Hf}_y$ are shown in Fig.2. An endmember, $\text{Na}_{1.5}\text{Zr}_2\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$ ($y=0$), showed a conductivity of $3.7 \times 10^{-3} \text{ Scm}^{-1}$ at 300°C, and an activation energy of 38.5 kJmol^{-1} . These are consistent with the previous results [$8 \times 10^{-4} \text{ Scm}^{-1}$, 28 kJmol^{-1}]¹¹. On the first approximation in the $\text{Zr}_{2-y}\text{Ti}_y$ and $\text{Hf}_{2-y}\text{Ti}_y$ systems, conductivities decrease about 1.5 orders of magnitude with the increase of Ti^{4+} ion content. Activation energies increase from 35 to 50 kJmol^{-1} with the increase of Ti^{4+} ion content in both cases. On the other hand, a shallow concave and convex were observed in the composition dependence on the conductivity and the activation energy, respectively, in $\text{Zr}_{2-y}\text{Hf}_y$ system. This dependence is rather interesting because of the small difference between Zr^{4+} and Hf^{4+} ionic radii. However, it should be described as independence on the first approximation within a experimental error margin.

It was clearly observed that smaller cell volume gave lower conductivity and

Fig.2. Variation of conductivity (σ) at 300°C versus composition (y) in the ○: $\text{Zr}_{2-y}\text{Ti}_y$, ●: $\text{Hf}_{2-y}\text{Ti}_y$ and □: $\text{Zr}_{2-y}\text{Hf}_y$ systems.

Fig.3. Variation of porosity (Pr) versus composition (y) in the ○: $\text{Zr}_{2-y}\text{Ti}_y$, ●: $\text{Hf}_{2-y}\text{Ti}_y$ and □: $\text{Zr}_{2-y}\text{Hf}_y$ systems.

higher activation energies in the $\text{Zr}_{2-y}\text{Ti}_y$ and $\text{Hf}_{2-y}\text{Ti}_y$ systems. These results show that the bottleneck size would be made small and thus the potential barrier for Na^+ ion conduction would be higher in the Ti^{4+} ion rich compound.

The observed conductivity in sintered pellets is usually composed of bulk conductivity (σ_b) and grain boundary conductivity (σ_{gb}). All the pellets in our experiments showed a relatively large fraction of σ_{gb} in the observed overall conductivity, because a capacity of 10–100pF/cm in a parallel RC element equivalent circuit, which is a typical value for grain boundary conduction¹²⁾. Figure 3 shows the composition dependence of porosity, defined as $[1 - D_b/D_c] \times 100$, where D_b is bulk density and D_c is calculated density. The porosity of the pellet should be an indication of the degree of sintering. Porosity minima were observed in the range $y=0.5-1.0$ in the $\text{Zr}_{2-y}\text{Ti}_y$ and $\text{Hf}_{2-y}\text{Ti}_y$ systems. We expect that the pellet with a higher degree of porosity shows lower conductivity if σ_{gb} is a large fraction of observed overall conductivity. Experi-

mental results did not show this tendency. The conductivity around $y=2.0$ is, therefore, significantly lower than that of $y=0$. In the system of $\text{Zr}_{2-y}\text{Hf}_y$ the dependence of cell volume, electrical conductivity and porosity on Hf^{4+} ion content are not so large but the tendency seems to be consistent with our expectation.

In conclusion, Ti^{4+} ion substitution for Zr^{4+} ion or Hf^{4+} ion decreases cell volume and conductivity. This is attributable to the smaller size of bottleneck in NASICON framework. On the other hand, Hf^{4+} ion substitution for Zr^{4+} ion show a few effect against cell volume and conductivity because of the similar ionic radii.

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