A Discovery of Tetravalent Ge^{4+} Ion Conduction in Solids

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Tetravalent Ge^{4+} ion conduction in solids was first demonstrated by selecting a NASICON-type $GeNb(PO_4)_3$ solid and partially replacing P^{5+} ion in $GeNb(PO_4)_3$ with Si^{4+} ion to expand the crystal lattice, which allows for realization of a Ge^{4+} ion with high valence and electronegativity. Among the $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ solids prepared, it was found that $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ ($x = 0.1$) solid showed the highest Ge^{4+} ion conductivity.

Ion conduction in solids generally depends on the strength of the interaction between the mobile ion and surrounding counter ions in the crystal structure. Therefore, the higher the valence state of the mobile cations, the lower the ion conductivity of the solid, because of the strong electrostatic interaction. In addition, cations with high electronegativity have not been explored as conducting species in solids because such cations should be lattice forming by covalently bonding to anionic species in solids. To date, the cation species known to conduct in solids have been those possessing low electronegativity such as monovalent alkali metal ions (Pauling's scale of electronegativity [EN] ≤ 0.98),[1–3] divalent alkaline earth metal ions (EN ≤ 1.0),[4,5] trivalent Al^{3+} (EN $= 1.61$)[6] and rare earth ions (EN ≤ 1.36),[7,8] and tetravalent Zr^{4+} (EN $= 1.33$),[9–11] Hf^{4+} (EN $= 1.3$),[12] and Ti^{4+} (EN $= 1.54$)[13] ions. There is, however, an exception of Ag^+ ion (EN $= 1.93$)[14,15] in the α-AgI structure, which can be regarded as an intermediate structure between that of a typical ionic solid in which every lattice site is occupied and that of a typical ionic liquid in which both anions and cations are disordered.

There is another crystal structure suitable for ion conduction in solids, that is, three-dimensional networks. Recently, we have successfully demonstrated tetravalent M^{4+} (M = Zr, Hf, and Ti) cation conducting $MNb(PO_4)_3$ solids[9–13] with NASICON (Na^+ superionic conductor)-type three-dimensional network structure which is built by NbO_6 octahedron and PO_4 tetrahedron by sharing the corner oxygen and has large open space for M^{4+} ion conduction. Since O^{2-} ions are strongly attracted to Nb^{5+} and P^{5+} in this structure, it is expected that the bonding between M^{4+} and surrounding O^{2-} ions is effectively reduced.

In this letter, we focused on the tetravalent Ge^{4+} ion with electronegativity of 2.01 as a target conducting tetravalent cation in solids. While Ge is a well-known glass-forming element due to its high electronegativity, Ge^{4+} ion also has a possibility for migration in NASICON-type structures in which other high-valent cations (such as Nb^{5+} and P^{5+}) form the rigid skeleton structure. For realizing Ge^{4+} ion conduction in solids, we selected NASICON-type $GeNb(PO_4)_3$ as the mother solid similar to the case of Zr^{4+}, Hf^{4+}, and Ti^{4+} ion conductors.[9–13] In addition, we partially replaced the P^{5+} (ionic size = 0.031 nm [coordination number (CN): 4][16]) site with larger Si^{4+} (0.040 nm [CN: 4][16]) ion for expanding the crystal lattice, which directly influenced the expansion of conduction pathways in the structure, and the Ge^{4+} ion conducting properties in the $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ solids were investigated.

$Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ ($x = 0.0$–0.3) were prepared by a sol–gel method. Stoichiometric amounts of ethanol solution of $1\,mol\,L^{-1}$ $GeCl_4$, $0.1\,mol\,L^{-1}$ $NbCl_5$, and $0.1\,mol\,L^{-1}$ $Si(OC_2H_5)_4$ were mixed. After homogenization of the ethanol solution, $(NH_4)_2HPO_4$ dissolved in $3\,mol\,L^{-1}$ nitric acid was added dropwise into the mixed ethanol solution to obtain yellow precipitates. The solution was stirred at 130 °C for 24 h, and then the ethanol and water were vaporized at 130 °C. The powder obtained was calcined at 600 °C for 6 h and then at 1100 °C for 12 h in air. The samples obtained were identified by X-ray powder diffraction (XRD) analysis using Cu Kα radiation (MultiFlex, Rigaku). The XRD data were collected by the step scanning method in the 2θ range from 10 to 70° with a step width of 0.04°, and the lattice volume of the samples was calculated by refining the XRD patterns using α-Al_2O_3 as a standard. The $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ powders were pelletized and sintered at 1100 °C for 12 h in air. The electrical conductivity was measured for the sintered pellet with Pt layer on both center surfaces by a complex impedance method in the frequency region from 5 Hz to 13 MHz (precision LCR meter 4192A, Hewlett Packard). DC electrolysis of the sintered pellet was carried out by applying a DC voltage of 6 V for 360 h at 800 °C in air using ion-blocking platinum bulk electrodes, and XRD analysis and line electron probe microanalysis (EPMA; EPMA-1500, Shimadzu) were performed for the electrolyzed sample.

From the XRD analysis of the $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ ($x = 0.0$–0.3) solids, it was clear that single phase of the NASICON-type structure was obtained for the samples with $x \leq 0.1$ and that the lattice volume linearly expanded in this compositional region (Supporting Information, Figures S1 and S2),[17] suggesting that the P^{5+} ion site in $GeNb(PO_4)_3$ was partially substituted with larger Si^{4+} ion. On the other hand, the samples with $x > 0.1$ were a mixture of NASICON-type phosphate, GeP_2O_7, and SiO_2 without any lattice expansion of the NASICON-type phase compared to the sample with $x = 0.1$. These results clearly indicate that the solid solution limit of Si^{4+} into P^{5+} sites in $GeNb(PO_4)_3$ is $x = 0.1$.

The compositional dependence of the electrical conductivity at 600 °C for the $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ solids is presented in Figure 1. Among the single phase samples ($x \leq 0.1$), the conductivity increased with Si content (x) up to 0.1 because of the lattice expansion of the NASICON-type phase, and the conductivity of the sample with $x = 0.1$ was ca. 3.3 times as high as that of $GeNb(PO_4)_3$ ($x = 0.0$). In contrast, the conductivity of the samples with $x > 0.1$ monotonically decreased due to the appearance of impurity phases of GeP_2O_7 and SiO_2.

For identifying the conducting species in the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid which showed the highest conductivity among the prepared solids, we investigated the time dependence

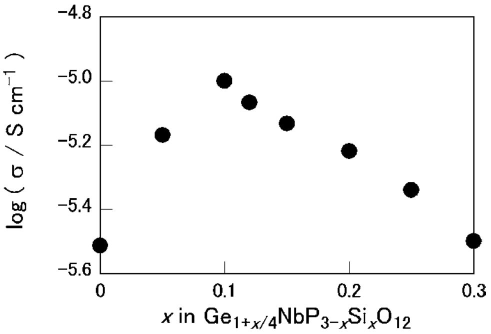

Figure 1. Compositional dependence of the conductivity at 600 °C for the $Ge_{1+x/4}NbP_{3-x}Si_xO_{12}$ solid.

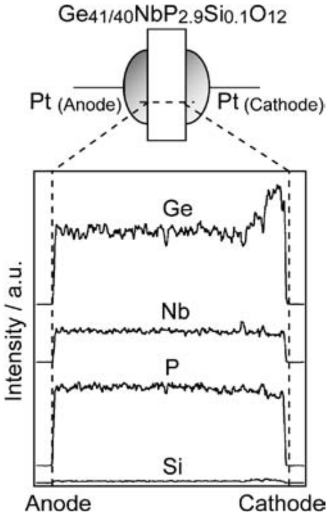

Figure 2. Results of EPMA line analysis for the electrolyzed $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid.

of the σ_{DC}/σ_{AC} ratio in oxygen and helium atmospheres. The ratios in both atmospheres abruptly reduced and the values were below 0.01 after 30 min (Supporting Information, Figure S3),[17] clearly indicating that the cation transference number was higher than 0.99. To directly identify the conducting cation species, we carried out the DC electrolysis of the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid by applying a DC voltage of 6 V for 360 h at 800 °C in air for the demonstration of Ge^{4+} ion conduction. Figure 2 shows the results of the EPMA line analysis of the sample pellet after DC electrolysis. A clear segregation of Ge was recognized near the cathodic surface from the EPMA line analysis of the electrolyzed sample pellet, while other cations distributed homogeneously over the sample. Furthermore, GeO_2 formation was clearly observed only at the cathodic surface of the electrolyzed sample (Supporting Information, Figure S4).[17] These results explicitly indicate that only Ge^{4+} ions migrated in the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid by DC electrolysis and deposited at the cathodic surface. Consequently, Ge deposited was oxidized in air atmosphere at the cathodic surface. From the results mentioned above, it was found that the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid is a Ge^{4+} ion conducting solid electrolyte.

Temperature dependencies of the Ge^{4+} ion conductivity for the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid is presented in Figure 3 with the corresponding data for $GeNb(PO_4)_3$. The activation energy for ion conduction in $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ (36.1 kJ mol^{-1}) is lower than that in $GeNb(PO_4)_3$ (51.1 kJ mol^{-1}). The enhancement in conductivity and the reduction in activation energy might be mainly caused by the lattice expansion by doping larger Si^{4+} into P^{5+} sites, realizing both the extension of Ge–O bonding and the expansion of the conducting pathway.

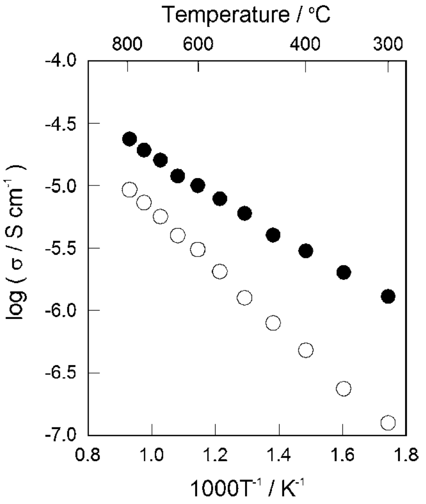

Figure 3. Temperature dependencies of the ion conductivity for the $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ (●) and $GeNb(PO_4)_3$ (○).

In conclusion, we have successfully developed a Ge^{4+} ion conducting $Ge_{41/40}NbP_{2.9}Si_{0.1}O_{12}$ solid for the first time by strictly selecting the NASICON-type structure and by intentionally expanding the lattice size by partially substituting the P^{5+} site with Si^{4+} ion in $GeNb(PO_4)_3$.

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17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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