

problem by designing a device that combines a metal-dielectric-metal (MDM) sandwich structure with a plasmonic crystal. The MDM structure, made from 200-nm-thick metal outer layers and a 12-nm-thick dielectric inner layer, provides planar plasmonic light confinement. It is pierced with a two-dimensional hexagonal array of 450-nm-diameter holes spaced at 500 nm intervals, providing lateral plasmonic crystal light confinement. The structure also contains a detection region that consists of a single defect in the crystal with a volume of only 15 zepto-

liters (40 nm diameter, 12 nm thick). Using finite-difference time-domain simulations, the team showed that the extremely small detection volume leads to a high Purcell factor (measuring the optical-molecular interaction strength) of  $4.8 \times 10^6$ , more than an order of magnitude higher than the best photonic crystals reported to date. However, the structure also displays a wide spectral bandwidth of 7.4 THz centered around  $3.45 \mu\text{m}$ , the wavelength region of interest for many molecular vibrational states, enabling robust molecular spectral fingerprinting. Finally, the sim-

ulations showed that it should be relatively easy to couple light into and out of the device from a direction orthogonal to the MDM plane, while simultaneously flowing gas or liquid through the defect. The team said that the device's behavior would be relatively insensitive to manufacturing errors within typical tolerances, as well as some environmental effects. Given these results, devices based on a metal-dielectric-metal/plasmonic crystal structure may someday form the basis for practical optical single-molecule detection systems.

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### Ionic Conduction of Tetravalent Ti Ion Observed in NASICON-Type Crystals Modified by Introduction of High-Valence Elements

High ionic conductivity in solid electrolytes has been demonstrated, up to recently, for mono-, di-, and trivalent conducting species. Tetravalent cations have been considered extremely poor migrating species in solids because of their strong electrostatic interaction with surrounding anions. However, this strong interaction can be weakened by the introduction in the structure of cations with higher valences, since they will attract the anionic species more strongly than the tetravalent cation, enabling its migration in the solid lattice. N. Nunotani, S. Tamura, and N. Imanaka from Osaka University, Japan, have demonstrated, by applying this strategy, high ionic conduction of  $\text{Ti}^{4+}$  in NASICON-type  $\text{TiNb}(\text{PO}_4)_3$ , and  $\text{Ti}(\text{Nb}_{1-x}\text{W}_x)_{5/(5+x)}(\text{PO}_4)_3$  structures. NASICON ( $\text{Na}^+$  super-ionic conductor) materials have three-dimensional networks that provide pathways for ionic migration.

As reported in the February 24 issue of *Chemistry of Materials* (DOI: 10.1021/cm803193k; p. 579), the researchers observed that, for crystals with W-content at  $x = 0.2$ , the electrical conductivity of  $\text{Ti}(\text{Nb}_{1-x}\text{W}_x)_{5/(5+x)}(\text{PO}_4)_3$  solids at  $800^\circ\text{C}$  increased substantially yielding a maximum value of conductivity of  $3.65 \times 10^{-4} \text{ S cm}^{-1}$ . For higher values of  $x$ , the researchers obtained a mixture of  $\text{TiP}_2\text{O}_7$  and  $\text{WO}_3$ . Because the electronegativity of  $\text{Ti}^{4+}$  is higher than those of  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$ , the ionic conductivity that the researchers measured in  $\text{TiNb}(\text{PO}_4)_3$  was lower than that measured previously in  $\text{ZrNb}(\text{PO}_4)_3$  and  $\text{HfNb}(\text{PO}_4)_3$ . However, in  $\text{Ti}(\text{Nb}_{0.8}\text{W}_{0.2})_{5.0/5.2}(\text{PO}_4)_3$ , the researchers said that the electrostatic interaction between  $\text{Ti}^{4+}$  and  $\text{O}^{2-}$  was reduced by the introduction of  $\text{W}^{6+}$ , and as a result,  $\text{Ti}(\text{Nb}_{0.8}\text{W}_{0.2})_{5.0/5.2}(\text{PO}_4)_3$  exhibited 2.2 times higher  $\text{Ti}^{4+}$  conductivity than  $\text{TiNb}(\text{PO}_4)_3$ .

To identify the conducting species in these solids, the researchers investigated the dependence of the ac conductivity with oxygen partial pressure at  $800^\circ\text{C}$ . They observed that above  $1 \times 10^{-11} \text{ Pa}$  the ac conductivities were constant. However, below this pressure the ac conductivity increased significantly because of the appearance of electronic conduction caused by the reduction of  $\text{Ti}^{4+}$ . The researchers also investigated the polarization behavior of this conductivity by measuring the dependence of the dc to ac conductivity ratio with time in oxygen and  $\text{CO-CO}_2$  gas mixture atmospheres. This proved that  $\text{O}^{2-}$  ions did not migrate in the sample. Furthermore, the

researchers directly demonstrated  $\text{Ti}^{4+}$  ion conduction in the  $\text{Ti}(\text{Nb}_{0.8}\text{W}_{0.2})_{5.0/5.2}(\text{PO}_4)_3$  solid by performing dc electrolysis at dc voltages higher than the decomposition voltage of this compound, that was established at 1.2 V. In this way, the researchers forced the conducting cation species only to migrate toward the cathode according to the potential gradient. After dc electrolysis, the researchers performed electron probe microanalysis line analysis of the electrolyzed pellet. They observed a clear segregation of Ti only near the cathodic surface, clearly demonstrating the ionic conduction of tetravalent Ti ion.

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