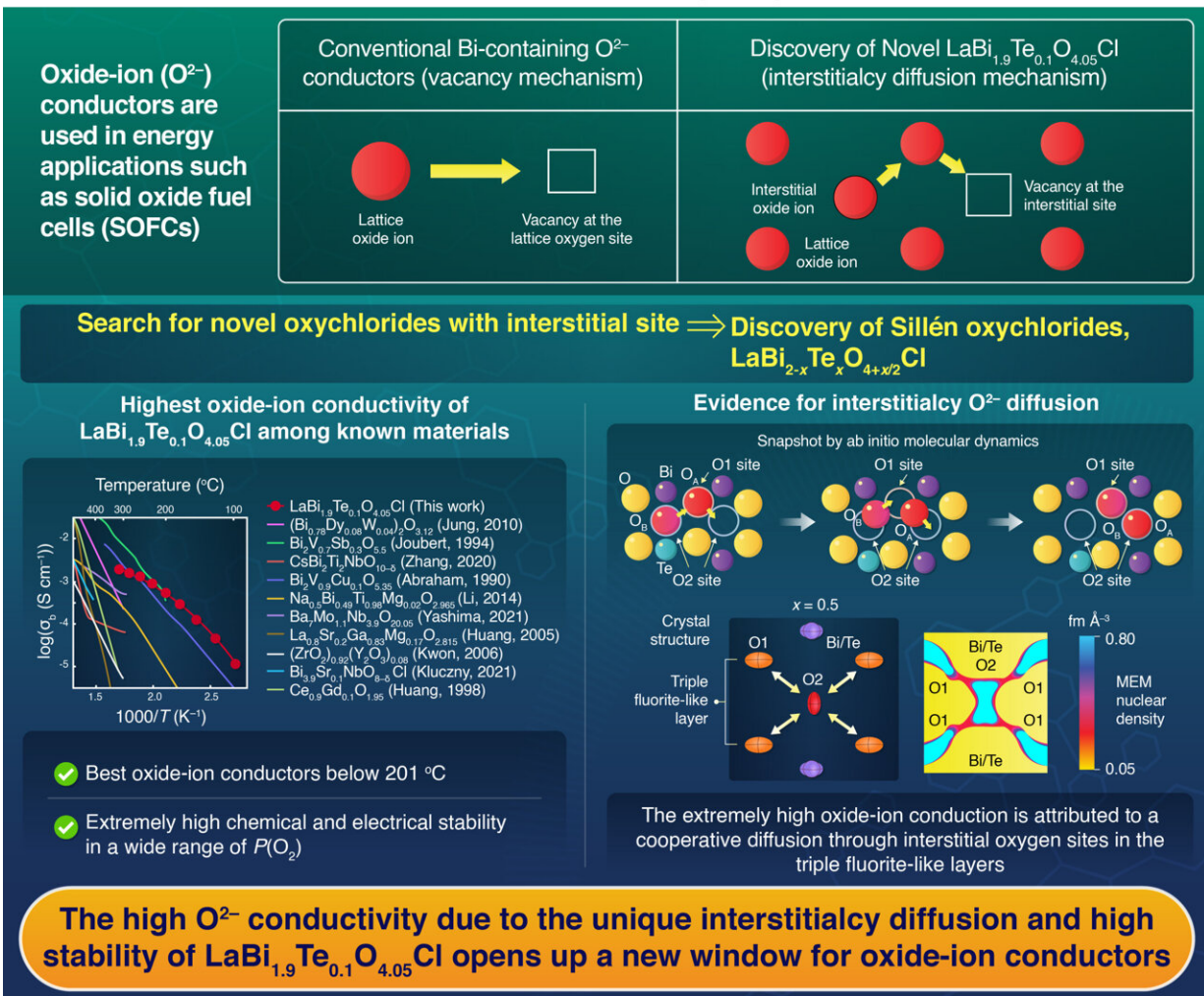


Novel oxychloride shows high stability and oxide-ion conduction through interstitial oxygen site

April 19 2023

High Oxide-ion Conductivity through the Interstitial Oxygen Site in Sillén Bi-containing Oxychlorides



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Yaguchi et al. (2023) | *Advanced Functional Materials* | 10.1002/adfm.202214082

Credit: Tokyo Tech

Solid oxide fuel cells (SOFCs) are a promising solution to the contemporary problem of the impending global energy crisis. SOFCs show high efficiency, lower emissions, and have low operating costs, making them an ideal power source for a fossil fuel-free society.

Conventional SOFCs with yttria-stabilized zirconia (YSZ) electrolytes have high operating temperatures (700°C–1000°C), and their widespread adoption has been limited by their degradation issues and high cost. Therefore, there is a need to search for new materials exhibiting high conductivities and stability at low temperatures (100°C–300°C). While some bismuth(Bi)-containing materials exhibit high oxide-ion conductivities through the conventional vacancy diffusion mechanism, they are not very stable under reduced atmospheres. As an alternative, the interstitialcy migration mechanism, involving the knock-on motion of interstitial and lattice oxide ions, has attracted much attention. However, they are rarely observed in Bi-containing materials.

A team of researchers from Japan led by Prof. Masatomo Yashima of Tokyo Institute of Technology (Tokyo Tech) put their heads together to find a solution to these problems. In their recent breakthrough published in *Advanced Functional Materials*, the team reported a new Bi-containing compound, $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$, where the oxide ions migrate via the interstitialcy mechanism. The team demonstrated that $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$ exhibits both high stability and a high oxide-ion conductivity that is superior to those of even the best oxide-ion conductors at low temperatures (below 201°C).

When asked how the team was able to discover $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$, Prof. Yashima explains, "Most known Bi-containing materials exhibit high oxide-ion conductivities via the conventional vacancy diffusion mechanism. The alternative mechanism, interstitialcy diffusion, is rare in these materials. Thus, we specifically searched for Bi-containing materials with interstitial oxygen site that could enable the interstitialcy diffusion."

The interstitial oxygen site refers to the empty space within a crystal structure the oxide ions partially occupy. Prof. Yashima's group selected a Bi-containing Sillén oxychloride, $\text{LaBi}_2\text{O}_4\text{Cl}$, with a triple fluorite-like layer to ensure the presence of such interstitial oxygen sites. They then partially substituted the Bi^{3+} cation with a high valence dopant, tellurium (Te) cation Te^{4+} , in the Sillén phase $\text{LaBi}_{2-x}\text{Te}_x\text{O}_{4+x/2}\text{Cl}$. The [chemical composition](#), $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$ ($x = 0.1$ in $\text{LaBi}_{1-x}\text{Te}_x\text{O}_{4+x/2}\text{Cl}$), was then chosen for detailed experimental and computational studies since the bulk conductivity of $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$ was the highest among those of all the other compositions, i.e., $\text{LaBi}_{2-x}\text{Te}_x\text{O}_{4+x/2}\text{Cl}$ ($0 \leq x \leq 0.2$).

The team found that $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$ exhibits high chemical and electrical stability at 400°C in a wide oxygen partial pressure region between 10^{-25} to 0.2 atm, as well as a high chemical stability in CO_2 , wet H_2 in N_2 , and air with natural humidity. Further, $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$ demonstrated a high oxide-ion conductivity of $2.0 \times 10^{-2} \text{ S cm}^{-1}$ at 702°C . The bulk conductivity of the material was significantly higher than those of the best oxide-ion conductors such as $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$ at temperatures between 96°C – 201°C .

To elucidate the mechanism underlying the high oxide-ion conduction, the team performed neutron-diffraction experiments, ab initio molecular dynamics simulations, and DFT calculations. The results indicated that the extremely high oxide-ion conduction is explained by an interstitialcy

migration of oxide ions through the lattice and interstitial sites, which is a rare occurrence in Bi-containing materials.

The discovery of the high oxide ionic conductivity along with high chemical and electrical stability of $\text{LaBi}_{1.9}\text{Te}_{0.1}\text{O}_{4.05}\text{Cl}$, and the unique mechanism underlying the high conductivity will open door to further research on Bi-containing compounds and Sillén phases, and eventually to high-performance SOFC electrolytes at low temperatures.

"There were studies on the photocatalysis and luminescence of Sillén phases in the research literature. In our study, we have now demonstrated that Sillén Bi-containing oxychlorides can also act as promising electrolytes for SOFCs and could contribute to the fuel cell revolution," concludes Prof. Yashima.

More information: High Oxide-ion Conductivity Through the Interstitial Oxygen Site in Sillén Oxychlorides, *Advanced Functional Materials* (2023). [DOI: 10.1002/adfm.202214082](https://doi.org/10.1002/adfm.202214082)

Provided by Tokyo Institute of Technology

Citation: Novel oxychloride shows high stability and oxide-ion conduction through interstitial oxygen site (2023, April 19) retrieved 24 April 2024 from <https://phys.org/news/2023-04-oxychloride-high-stability-oxide-ion-interstitial.html>

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