

PRESS RELEASE

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Headline: Apatite-Type Materials without Interstitial Oxygens Show High Oxide-Ion Conductivity by Overbonding

(Tokyo, May 16) **Scientists at Tokyo Institute of Technology; Nagoya Institute of Technology; National Institute of Technology, Niihama College; Neutron Science and Technology Center, The Comprehensive Research Organization for Science and Society (CROSS); and Japan Atomic Energy Agency have shown the overbonding of channel oxygens in La-rich apatite-type lanthanum silicates, rather than the presence of the interstitial oxygens, to be responsible for the high oxide-ion conductivity. This concept of “high oxide-ion conductivity by overbonding” opens the door for designing better ion conductors, which could be useful in energy conversion and environmental protection.**

Solid oxide electrolytes have been extensively studied due to their wide range of applications in solid oxide fuel cells (SOFCs), oxygen membranes, catalysts, and gas sensors. Electrolytes with high oxide-ion conductivity at temperatures below 600 °C are required to decrease the operation temperature of SOFCs. Professor Susumu Nakayama at National Institute of Technology, Niihama College has discovered in 1995 the extremely high oxide-ion conductivity in the intermediate temperature range below 600 °C, which has encouraged many researchers to study the structural origin of this phenomenon.

It was believed that the high oxide-ion conductivity of apatite-type materials is due to interstitial oxygens. However, in this novel study, Professor Masatomo Yashima, Dr. Kotaro Fujii at Tokyo Institute of Technology (Tokyo Tech), and their colleagues have shown that apatite-type materials contain Si vacancies, but not oxygen interstitials. The Si vacancies in the materials have originally been proposed by Professor Koichiro Fukuda at Nagoya Institute of Technology.

Through single-crystal neutron diffraction studies using the SENJU diffractometer installed at MLF, J-PARC facility (Figure 1), they were able to accurately determine the crystal structures of the apatite materials $\text{La}_{9.333}\text{Si}_6\text{O}_{26}$ and La-rich $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ (\square denotes Si vacancy) including occupancy factors, atomic displacement parameters, and spatial distributions of oxygen atoms. They also measured the density and oxide-ion conductivity of the two materials. In this work, $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ was selected because of its high oxide-ion conductivity.

By structure analyses using the diffraction data, the researchers found Si vacancies, no interstitial oxygens, and larger positional disorder of the oxide ion at the O4 site in the apatite channel as compared to the basic material $\text{La}_{9.333}\text{Si}_6\text{O}_{26}$ (Figure 2). The lower activation energy for the oxide-ion conduction along the c axis was found to be the main reason for the higher oxide-ion conductivity of $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ as compared to $\text{La}_{9.333}\text{Si}_6\text{O}_{26}$. The excess La yielded the overbonding of the O4 oxide ion in $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ as compared with $\text{La}_{9.333}\text{Si}_6\text{O}_{26}$, which led to higher oxide-ion mobility and conductivity of $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ with Si vacancies (Figure 2). Density measurements by the Archimedes method supported the presence of Si vacancies in $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$.

Thus, the researchers proposed that excess La cations are responsible for overbonded channel oxygens along the c axis, which leads to highly anisotropic atomic displacement and high oxygen mobility. Hence this novel concept of “high oxide-ion conductivity by overbonding” may be useful for designing better ion conductors.

Reference

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- Title of original paper: High oxide-ion conductivity by the overbonded channel oxygens in Si-deficient $\text{La}_{9.656}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ apatite without interstitial oxygens
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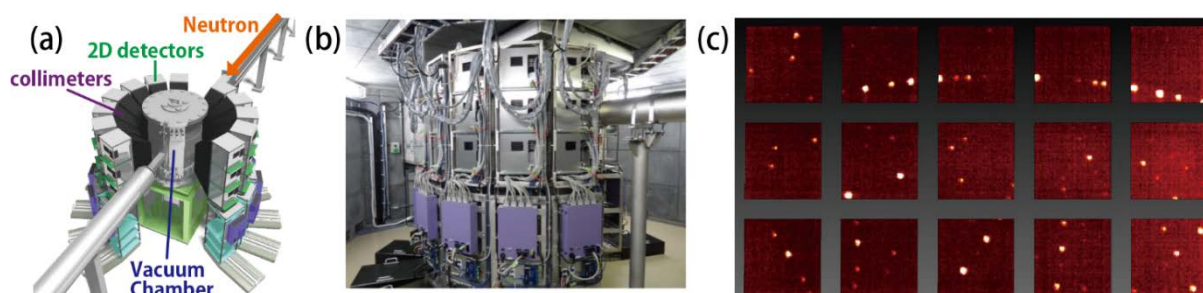


Figure 1 (a) A schematic figure and (b) a photograph of the SENJU diffractometer installed at the J- PARC facility. (c) Measured single-crystal neutron diffraction images.

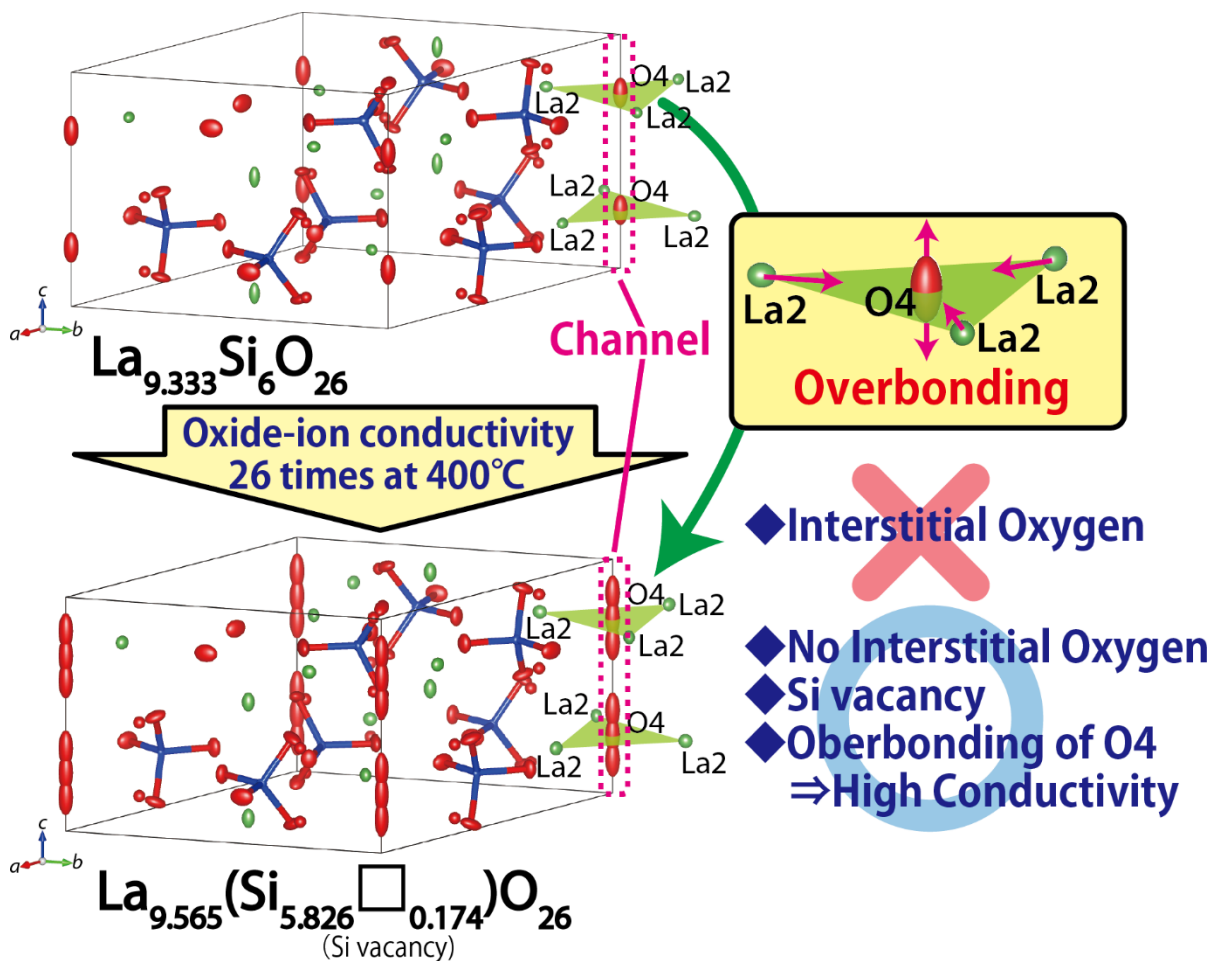


Figure 2 Crystal structures of the apatite-type oxide-ion conductors $\text{La}_{9.333}\text{Si}_6\text{O}_{26}$ and $\text{La}_{9.565}(\text{Si}_{5.826}\square_{0.174})\text{O}_{26}$ determined from the single-crystal neutron diffraction studies.

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