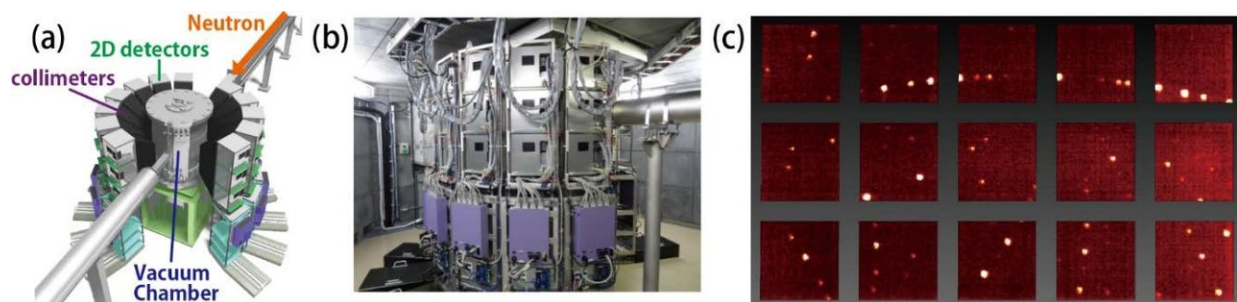


# Apatite-type materials without interstitial oxygens show high oxide-ion conductivity by overbonding

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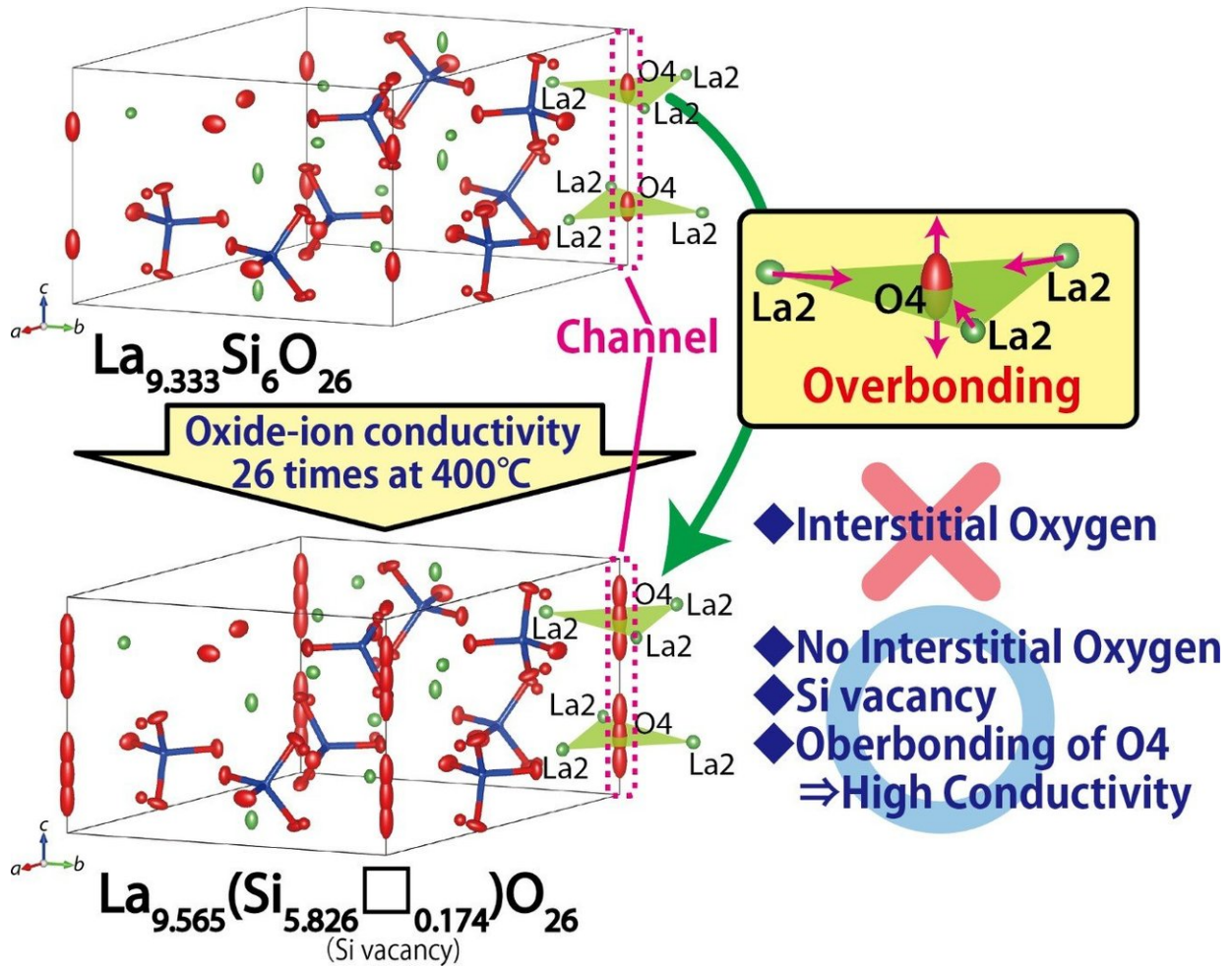
(a) A schematic figure and (b) a photograph of the SENJU diffractometer installed at the J-PARC facility. (c) Measured single-crystal neutron diffraction images. Credit: J-PARC

Scientists at Tokyo Institute of Technology and collaborators 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 degrees 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.



La<sub>9.333</sub>Si<sub>6</sub>O<sub>26</sub> and La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> determined from the single-crystal neutron diffraction studies. Credit: *Journal of Materials Chemistry A*

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 La<sub>9.333</sub>Si<sub>6</sub>O<sub>26</sub> and La-rich La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> (□ 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, La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> 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 O<sub>4</sub> site in the apatite channel as compared to the basic material La<sub>9.333</sub>Si<sub>6</sub>O<sub>26</sub> (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 La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> as compared to La<sub>9.333</sub>Si<sub>6</sub>O<sub>26</sub>. The excess La yielded the overbonding of the O<sub>4</sub> oxide ion in La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> as compared with La<sub>9.333</sub>Si<sub>6</sub>O<sub>26</sub>, which led to higher oxide-ion mobility and conductivity of La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> with Si vacancies (Figure 2). Density measurements by the Archimedes method supported the presence of Si vacancies in La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub>.

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.

**More information:** Kotaro Fujii et al, High oxide-ion conductivity by the overbonded channel oxygens in Si-deficient La<sub>9.565</sub>(Si<sub>5.826</sub>□<sub>0.174</sub>)O<sub>26</sub> apatite without interstitial oxygens, *Journal of Materials Chemistry A* (2018). [DOI: 10.1039/C8TA02237B](https://doi.org/10.1039/C8TA02237B)

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