PRESS RELEASE

Source:
Tokyo Institute of Technology, Public Relations Section
Australian Nuclear Science and Technology Organisation

For immediate release: October 24, 2017

Subject line: Discovery of a new structure family of oxide-ion conductors “SrYbInO4”

(Tokyo, October 24) **Scientists at Tokyo Institute of Technology (Professor Masatomo Yashima and colleagues, Tokyo Tech) and Australian Nuclear Science and Technology Organisation (Dr. James R. Hester, ANSTO) have discovered a new structure family of pure oxide-ion conductors $SrYbInO_4$. This new material is expected to lead to the development of solid oxide fuel cells, sensors, and oxygen separation membranes. This study would give a clue to solve energy and environmental problems in future.**

Because some A_2BO_4-based materials such as $(Pr,La)_2(Ni,Cu,Ga)O_{4+\delta}$ exhibit high oxide-ion conductivity, scientists at Tokyo Tech have been exploring new structure families of $ABCO_4$-based materials as $BaRInO_4$, where R represents a rare earth element. Here, A, B, and C are cations located at different crystallographic sites, and A, B, and C in $ABCO_4$ correspond to A, A, and B, respectively, in A_2BO_4.

Many researchers have investigated the optical, electrical, and magnetic properties of $CaFe_2O_4$-type materials, but the $CaFe_2O_4$-type pure oxide-ion conductors have not been reported yet. Therefore, Professor Masatomo Yashima and colleagues synthesized a new $CaFe_2O_4$-type material, strontium ytterbium indium oxide, $SrYbInO_4$. They investigated its crystal structure from room temperature to 1273 K, its temperature and partial pressure dependence of electrical conductivity, and oxide-ion diffusion pathways. The occupancy factors are also carefully refined using not only conventional X-ray diffraction data but also time-of-flight (TOF) and angle-dispersive-type neutron and synchrotron X-ray diffraction data in order to obtain reliable results. They demonstrate a partial Yb/In occupational disorder in $SrYbInO_4$ through careful analyses of occupancy factors.

Prof. Yashima and colleagues have chosen the chemical composition $SrYbInO_4$, because it contains no transition-metal cation, which leads to less electronic conduction. Moreover, $SrYbInO_4$ was expected to have the $CaFe_2O_4$-type structure in the structure field map shown in Fig. 1. Ionic radii of Sr^{2+} and (Yb^{3+}, In^{3+}) are larger than those of Ca^{2+} and Fe^{3+}, thus the $SrYbInO_4$ is expected to have a lower activation energy for oxide-ion conductivity compared with $CaFe_2O_4$.

$SrYbInO_4$ was synthesized by a solid-state reaction. $SrYbInO_4$ was characterized through X-ray diffraction, chemical analysis, and thermogravimetric analysis. The band gap of $SrYbInO_4$ was also estimated using UV-vis reflectance spectra, which suggested that $SrYbInO_4$ is an electronic insulator. These results strongly suggested that $SrYbInO_4$ was a pure oxide-ion conductor.

Using neutron and synchrotron X-ray diffraction data and Rietveld method, Prof. Yashima and colleagues showed that $SrYbInO_4$ is a single orthorhombic phase with Yb/In occupational disordering at the *B* and *C* sites, and no vacancies at the cation and oxygen sites. Bond valence sums and DFT-based structural optimization indicated the validity of the refined crystal structure of $SrYbInO_4$. Therefore, the new material $SrYbInO_4$ is the first example of pure oxide-ion conductors with a $CaFe_2O_4$-type structure.

Further the temperature dependence of oxide-ion conductivity showed lower activation energy of $SrYbInO_4$ (1.76 eV) than that of $CaFe_2O_4$ (3.3 eV), which was supported also by the bond valence-based energy calculations. The lower activation energy is attributable to the larger bottleneck size for oxide-ion migration due to the larger ionic radii of Sr^{2+} and (Yb^{3+}, In^{3+}) than those of Ca^{2+} and Fe^{3+}, respectively.

Prof. Yashima and colleagues claimed that the oxide ion conductivity of $SrYbInO_4$ could be improved by doping, changing the degree of cation ordering and disordering, and using larger *A*, *B*, and *C* cations in the $ABCO_4$-structure, which leads to further lowering the activation energy and higher oxide-ion conductivity. The findings of this study may open new pathways in the development of $ABCO_4$-based ion conductors.

Reference

Authors:	Ayaka Fujimoto[1], Masatomo Yashima[1,*], Kotaro Fujii[1], James R. Hester[2]
Title of original paper:	New Oxide-Ion Conductor $SrYbInO_4$ with Partially Cation-Disordered $CaFe_2O_4$-Type Structure
Journal:	*The Journal of Physical Chemistry C*
DOI:	10.1021/acs.jpcc.7b07911
Affiliations:	[1] Department of Chemistry and Materials Science, Graduate School of Science and Engineering and Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-W4-17, O-okayama, Meguro-ku, Tokyo 152-8551, Japan [2] Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation (ANSTO), Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

*Corresponding author’s email: yashima@cms.titech.ac.jp

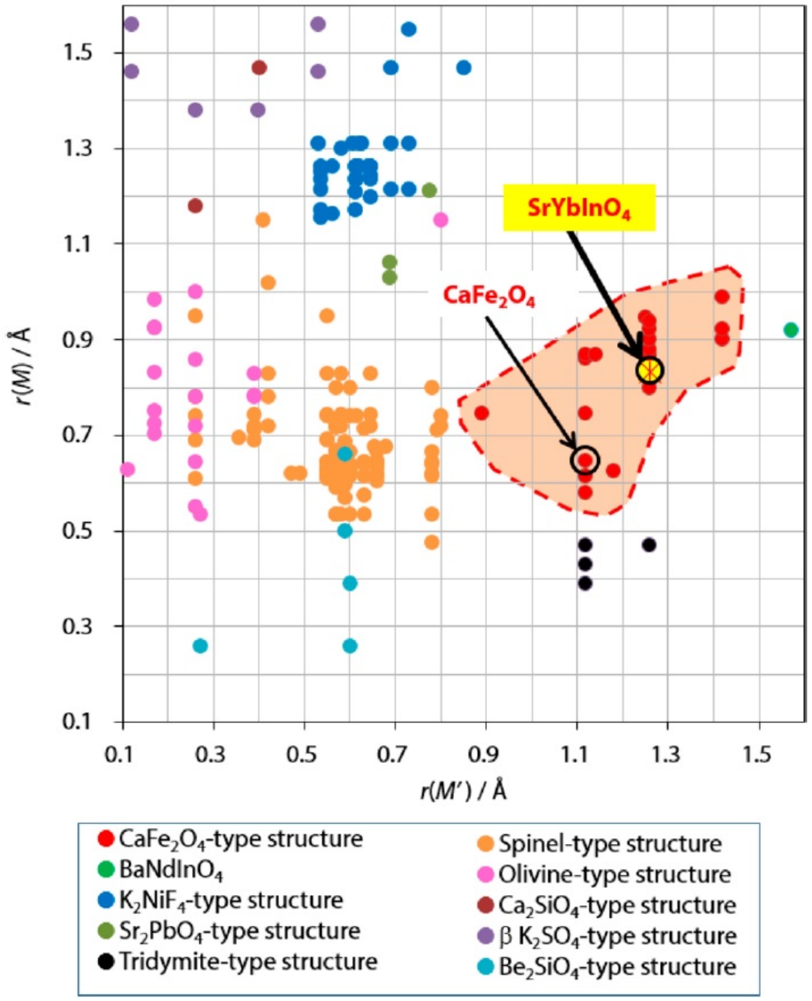

Figure 1. Structure Field Map of $M_2M'O_4$ Compounds.

The structure field map shows 209 different compositions of $M_2M'O_4$ compounds, with the red hatched area representing the CaFe$_2$O$_4$-type structure field. The newly synthesized compound SrYbInO$_4$ is shown within the CaFe$_2$O$_4$-type structure field. © American Chemical Society.

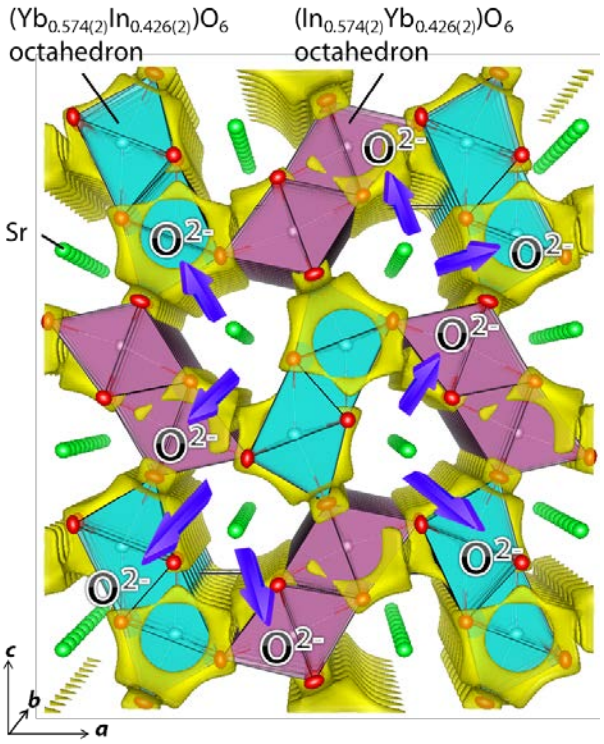

Figure 2. Refined Crystal Structure and Bond-Valence-Based Energy (BVE) Landscape of a test Oxide Ion of $SrYbInO_4$.

Yellow isosurface of the BVE at 0.8 eV suggests that the oxide ion migrates in the *b* direction along the edge/surface of light blue purple octahedra BO_6 [B = $Yb_{0.574(2)}In_{0.426(2)}$] and purple octahedra CO_6 [C = $In_{0.574(2)}Yb_{0.426(2)}$] where the number in the parenthesis is the estimated standard deviation. © American Chemical Society.

Contact for science
Professor Masatomo Yashima
Department of Chemistry,
Tokyo Institute of Technology
Email: yashima@cms.titech.ac.jp
Website: http://www.chemistry.titech.ac.jp/~yashima/e
+81-3-5734-2225

Contact for Tokyo Tech press
Emiko Kawaguchi
Public Relations Section,
Tokyo Institute of Technology
Email: media@jim.titech.ac.jp
+81-3-5734-2975

Contact for ANSTO press
Philip McCall
ANSTO Media Advisor
Email: pmccall@apa.net.au
+61 (0)438 619 987

About Tokyo Institute of Technology
Tokyo Institute of Technology stands at the forefront of research and higher education as the leading university for science and technology in Japan. Tokyo Tech researchers excel in a variety of fields, such as material science, biology, computer science and physics. Founded in 1881, Tokyo Tech has grown to host 10,000 undergraduate and graduate students who become principled leaders of their fields and some of the most sought-after scientists and engineers at top companies. Embodying the Japanese philosophy of “monotsukuri,” meaning technical ingenuity and innovation, the Tokyo Tech community strives to make significant contributions to society through high-impact research.
Website: http://www.titech.ac.jp/english/