

International Research Center for Elements Science – Advanced Solid State Chemistry –

<https://www.scl.kyoto-u.ac.jp/~shimakgr/indexE.html>



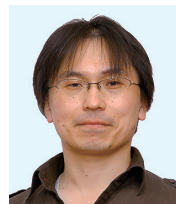
Prof
SHIMAKAWA, Yuichi
(D Sc)



Assoc Prof
KAN, Daisuke
(D Sc)



Assist Prof
GOTO, Masato
(D Sc)



Techn Staff
ICHIKAWA, Noriya
(D Eng)

Students

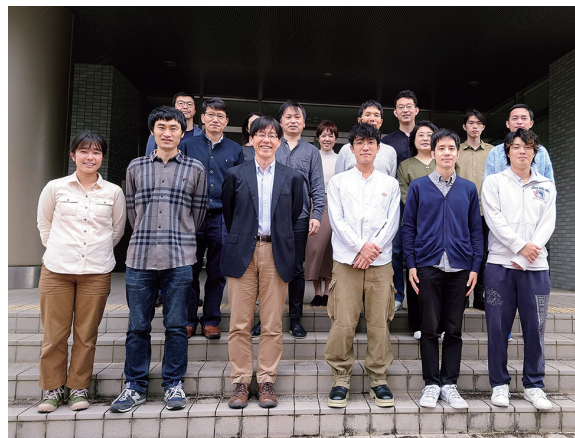
IHOSHI, Makoto (D2) XIE, Lingling (D2) ITO, Mayuri (M1)
ISODA, Yosuke (D2) CHEN, Chen (D2) FUJI, Souta (M1)
SHEN, Yufan (D2) WATANABE, Rei (D1)

Scope of Research

Transition metal oxides have a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides are used in current electronic devices. Our research mainly focuses on perovskite-structured transition metal oxides with novel functional properties due to complex couplings between their lattices, charges and spins. We are currently exploring such functional oxides with advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth.

KEYWORDS

Solid State Chemistry Functional Metal Oxides
High Pressure Synthesis Epitaxial Thin Film Growth
Heterointerface



Recent Selected Publications

Iihoshi, M.; Goto, M.; Kosugi, Y.; Shimakawa Y., Cascade Charge Transitions of Unusually High and Mixed Valence Fe^{3.5+} in the A-Site Layer-Ordered Double Perovskite SmBaFe₂O₆, *J. Amer. Chem. Soc.*, **145**, 10756-10762 (2023).
Kamada, T.; Ueda, T.; Fukuura, S.; Yumura, T.; Hosokawa, S.; Tanaka, T.; Kan D.; Shimakawa Y., Ultralong Distance Hydrogen Spillover Enabled by Valence Changes in a Metal Oxide Surface, *J. Am. Chem. Soc.*, **145**, 1631-1637 (2023).
Chen, C.; Kosugi, Y.; Goto, M.; Shimakawa Y., Thermal Properties and Phase Transition Behaviors of Possible Caloric Materials Bi_{0.95}Ln_{0.05}NiO₃, *J. Mater. Chem. A*, **10**, 15389-15393 (2023).
Shimakawa Y.; Kosugi Y., Giant Caloric Effects in Charge-Spin-Lattice Coupled Transition-Metal Oxides, *J. Mater. Chem. A*, **11**, 12695-12702 (2023).
Isoda, Y.; Kan, D.; Majima, T.; Shimakawa Y., Orientation-Dependent Electrochemical Reduction and Proton Evolution in the Oxygen-Deficient Perovskite SrFeO_{2.5+y}, *Appl. Phys. Express*, **16**, 015506/1-5 (2023).

Cascade Charge Transitions of Unusually High and Mixed Valence Fe^{3.5+} in the A-Site Layer-Ordered Double Perovskite SmBaFe₂O₆

Phase transitions caused by relieving of charge instability are one of the most important and interesting phenomena in solid state chemistry and condensed matter physics. A typical example was found in Fe₃O₄, and the transition is often called the Verwey transition. It occurs when the instability of a mixed valence state of Fe^{2.5+} at the B site of the spinel-type crystal structure is relieved, resulting in charge-ordered states of Fe²⁺ and Fe³⁺, with an accompanying metal-to-insulator transition. Another phase transition caused by relieving charge instability is seen in compounds containing an unusually high valence state of ions. The typical example is Fe⁴⁺ seen in the perovskite-type structured CaFeO₃. Fe⁴⁺ in CaFeO₃ shows charge disproportionation to Fe³⁺ and Fe⁵⁺ in a rock-salt manner, which accompanies a metal-to-insulator transition. We are then very interested in the phase transition behaviors of a compound containing ions in both unusually high and mixed valence states. To prepare such a compound, in this work, we used the A-site layer-ordered oxygen-deficient precursor SmBaFe₂O₅, which contains the mixed valence state of Fe^{2.5+} ions. By topochemically oxidizing the compound to fully incorporate oxygen ions into the vacant sites, the A-site layer-ordered double perovskite SmBaFe₂O₆ with the unusually high and mixed valence state of Fe^{3.5+} was obtained. We have found that cascade phase transitions are induced in SmBaFe₂O₆ to relieve the charge instability, described as SmBaFe^{3.5+}₂O₆ → SmBa(Fe³⁺Fe⁴⁺)O₆ → SmBa(Fe³⁺Fe^{(4+δ)+}_{0.5}Fe^{(4+δ)+}_{0.5})O₆ → SmBa(Fe³⁺_{1.5}Fe⁵⁺_{0.5})O₆. The first Verwey-like charge-order transition occurred at 340 K and was accompanied by a significant structural change and a sudden increase in magnetic susceptibility. The following transition was the charge disproportionation of metastable Fe⁴⁺ to Fe³⁺ and Fe⁵⁺, and each of the spins resulted in the antiferromagnetic ground state.

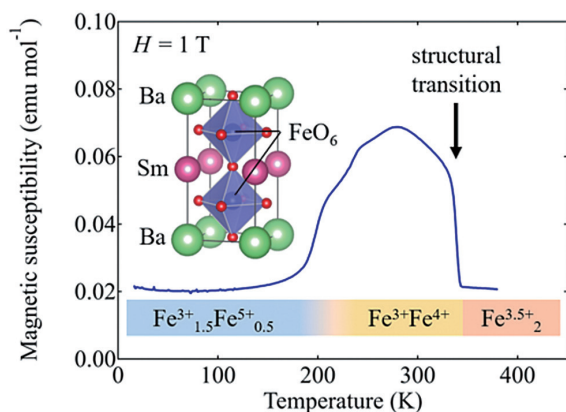


Figure 1. Crystal structure of the topochemically oxidized double perovskite SmBaFe₂O₆ and temperature dependence of magnetic susceptibility of SmBaFe₂O₆.

Ultralong Distance Hydrogen Spillover Enabled by Valence Changes in a Metal Oxide Surface

The surface of metal oxides is a fertile platform for chemical reactions and an important subject of investigation. However, experimentally characterizing and understanding surface reactions are challenging, especially when hydrogen is involved in chemical reactions on oxides' surfaces. The occurrence of hydrogen spillover on oxide surfaces has been established since its discovery in 1964. Furthermore, this phenomenon has been utilized as a reaction route for producing functional materials. Nonetheless, the fundamental characteristics of hydrogen spillover remain elusive. This is because of experimental difficulties in observing hydrogen during chemical reactions. In addition, reaction systems utilizing hydrogen spillover are complex and not well defined. Delineating hydrogen reactions and diffusion on oxide surfaces therefore requires proper design and construction of model (or ideal) reaction systems without such complexities. Recent progress in nanometer-level material techniques enables the fabrication of well-defined model catalytic systems with separated functions. The model systems, consisting of epitaxial films of catalytic oxide supports and metal catalysts located at controlled positions on the supports' surfaces, are useful for evaluating various phenomena associated with (electro) chemical reactions. Since catalytic supports are reduced in the hydrogen spillover process, tracking hydrogen-spillover-induced changes in model systems enables the "visualization" of hydrogen. Here, in this study, we fabricated catalytic model systems based on Pd-loaded SrFeO_x (x~2.8) epitaxial films and investigated hydrogen spillover. We show that hydrogen spillover on the SrFeO_x support extends over long distances (~600 μm). Furthermore, the hydrogen-spillover-induced reduction of Fe⁴⁺ in the support yields large energies (as large as 200 kJ/mol), leading to the spontaneous hydrogen transfer and driving the surprisingly ultralong hydrogen diffusion. These results show that the valence changes in the supports' surfaces are the primary factor determining the hydrogen spillover distance.

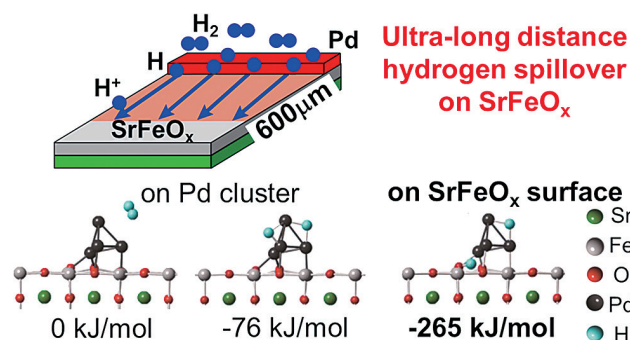


Figure 2. Schematic drawing of ultralong distance hydrogen spillover on SrFeO_x.