

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

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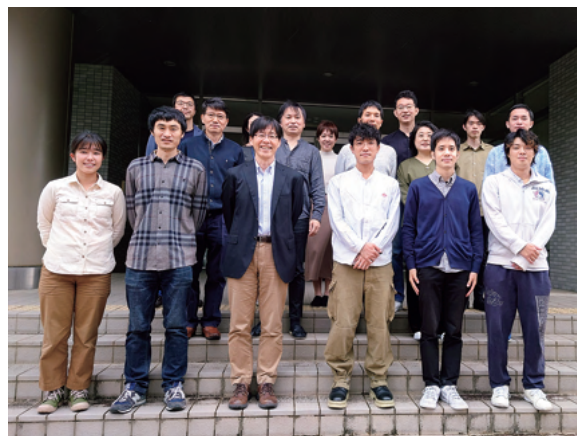
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Scope of Research

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 $\text{Fe}^{3,5+}$ in the A-Site Layer-Ordered Double Perovskite $\text{SmBaFe}_2\text{O}_6$, *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 $\text{Bi}_{0.95}\text{Ln}_{0.05}\text{NiO}_3$, *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 $\text{SrFeO}_{2.5+y}$, *Appl. Phys. Express*, **16**, 015506/1-5 (2023).

Cascade Charge Transitions of Unusually High and Mixed Valence $\text{Fe}^{3.5+}$ in the A-Site Layer-Ordered Double Perovskite $\text{SmBaFe}_2\text{O}_6$

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 Fe_3O_4 , and the transition is often called the Verwey transition. It occurs when the instability of a mixed valence state of $\text{Fe}^{2.5+}$ at the B site of the spinel-type crystal structure is relieved, resulting in charge-ordered states of Fe^{2+} and Fe^{3+} , 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 Fe^{4+} seen in the perovskite-type structured CaFeO_3 . Fe^{4+} in CaFeO_3 shows charge disproportionation to Fe^{3+} and Fe^{5+} 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 $\text{SmBaFe}_2\text{O}_5$, which contains the mixed valence state of $\text{Fe}^{2.5+}$ ions. By topochemically oxidizing the compound to fully incorporate oxygen ions into the vacant sites, the A-site layer-ordered double perovskite $\text{SmBaFe}_2\text{O}_6$ with the unusually high and mixed valence state of $\text{Fe}^{3.5+}$ was obtained. We have found that cascade phase transitions are induced in $\text{SmBaFe}_2\text{O}_6$ to relieve the charge instability, described as $\text{SmBaFe}^{3.5+}_2\text{O}_6 \rightarrow \text{SmBa}(\text{Fe}^{3+}\text{Fe}^{4+})\text{O}_6 \rightarrow \text{SmBa}(\text{Fe}^{3+}\text{Fe}^{(4-\delta)+}_{0.5}\text{Fe}^{(4+\delta)+}_{0.5})\text{O}_6 \rightarrow \text{SmBa}(\text{Fe}^{3+}_{1.5}\text{Fe}^{5+}_{0.5})\text{O}_6$. 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 Fe^{4+} to Fe^{3+} and Fe^{5+} , and each of the spins resulted in the antiferromagnetic ground state.

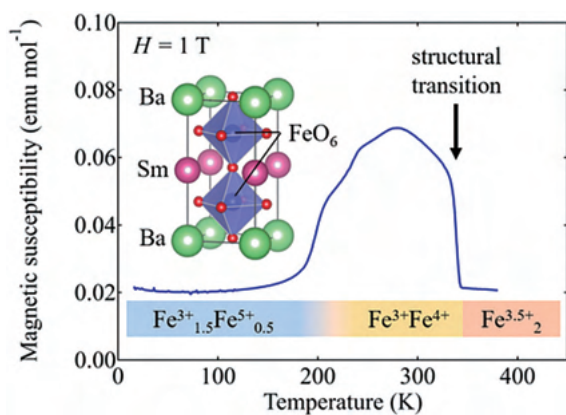


Figure 1. Crystal structure of the topochemically oxidized double perovskite $\text{SmBaFe}_2\text{O}_6$ and temperature dependence of magnetic susceptibility of $\text{SmBaFe}_2\text{O}_6$.

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 ($x \sim 2.8$) epitaxial films and investigated hydrogen spillover. We show that hydrogen spillover on the SrFeO_x support extends over long distances ($\sim 600 \mu\text{m}$). Furthermore, the hydrogen-spillover-induced reduction of Fe^{4+} 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.

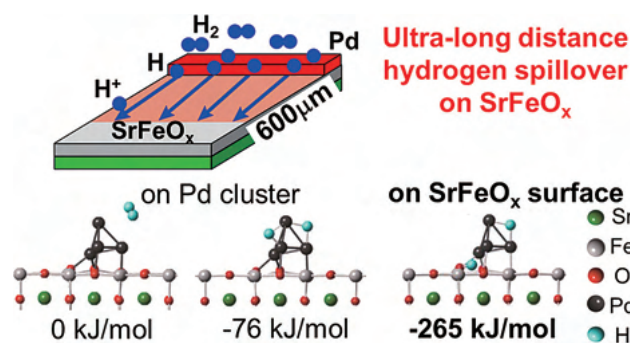


Figure 2. Schematic drawing of ultralong distance hydrogen spillover on SrFeO_x .