

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

KOSUGI, Yoshihisa (D3)
IIHOSHI, Makoto (D1)
ISODA, Yosuke (D1)

SHEN, Yufan (D1)
XIE, Lingling (D1)
CHEN, Chen (D1)

HOURLAI, Shinji (M2)
MAKINO, Momo (M2)
WATANABE, Rei (M2)

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

- Patino, M. A.; Romero F. D.; Koo, H. -J.; Avdeev, M.; Injac, S. D. A.; Goto, M.; Whangbo, M. -H.; Shimakawa, Y., Orthogonal Antiferromagnetism to Canted Ferromagnetism in $\text{CaCo}_3\text{Ti}_4\text{O}_{12}$ Quadruple Perovskite Driven by Underlying Kagome Lattices, *Commun. Mater.*, **3**, 51 (2022).
- Tan, Z.; Lussier, J. A.; Yamada, T.; Xu, Y.; Saito, T.; Goto, M.; Kosugi, Y.; Vrublevskiy, D.; Kanemitsu, Y.; Bieringer, M.; Shimakawa, Y., LiNbO_3 -Type Polar Antiferromagnet InVO_3 Synthesized under High-Pressure Conditions, *Angew. Chem. Int. Ed.*, **61**, e202203669 (2022).
- Kan, D.; Moriyama, T.; Aso R.; Horai, S.; Shimakawa, Y., Triaxial Magnetic Anisotropy and Morin Transition in $\alpha\text{-Fe}_2\text{O}_3$ Epitaxial Films Characterized by Spin Hall Magnetoresistance, *Appl. Phys. Lett.*, **120**, 112403 (2022).
- Isoda, Y.; Kan, D.; Ogura, Y.; Majima, T.; Tsuchiya, T.; Shimakawa, Y., Electrochemical Control and Protonation of the Strontium Iron Oxide SrFeO_y by Using Proton-Conducting Electrolyte, *Appl. Phys. Lett.*, **120**, 091601 (2022).
- Guo, H.; Patino, M. A.; Ichikawa N.; Saito, T.; Watanabe, R.; Goto, M.; Yang, M.; Kan D.; Shimakawa Y., Oxygen Release and Incorporation Behaviors Influenced by A-Site Cation Order/Disorder in $\text{LaCa}_2\text{Fe}_3\text{O}_9$ with Unusually High Valence $\text{Fe}^{3,67+}$, *Chem. Mater.*, **34**, 345-350 (2022).

Geometrical Spin Frustration and Monoclinic-Distortion-Induced Spin Canting in the Double Perovskites $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{and Eu}$) with Unusually High Valence Fe^{5+}

Exploring materials containing transition-metal ions with unusual valence states could lead to finding exotic properties and functionalities. Fe in oxides typically has valence states between +2 and +3, as seen in the Fe^{2+} of Wustite FeO , and in the Fe^{3+} of α -hematite $\alpha\text{-Fe}_2\text{O}_3$. Unusually high valence Fe^{5+} is much rare. Recently, we discovered a Fe^{5+} example in the B-site-ordered double perovskite $\text{La}_2\text{LiFeO}_6$, which is stable in the air. Importantly, Fe^{5+} in the B-site-ordered double perovskite structure makes a face-centered cubic (fcc.) arrangement of Fe^{5+} , and thus geometrically spin frustration arises if the magnetic interaction between the Fe^{5+} spins is antiferromagnetic.

After this discovery, we extended our material exploration to related B-site-ordered double perovskites $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{and Eu}$) and systematically studied the Fe^{5+} -spin frustration effects in the fcc lattice. Our experimental and theoretical results show the presence of most likely unusually high valence Fe^{5+} ions in all of the compounds. In particular, $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$) are the first examples adopting purely and octahedrally oxygen-coordinated Fe^{5+} . We also elucidated the structure-property relationships in the geometrically frustrated system. All of the compounds we synthesized were found to be highly frustrated due to the Fe fcc arrangements. In contrast, the crystal structure and magnetic ground state depend on the Ln ion. Indeed, while $\text{La}_2\text{LiFeO}_6$ adopts a rhombohedral structure, the others adopt monoclinic structures, and the monoclinic distortion largely increases for $\text{Ln} = \text{Sm}$ and Eu . Associated with the monoclinic distortion, only $\text{Ln} = \text{Sm}$ and Eu adopt spontaneous magnetization, which is most likely due to the Dzyaloshinskii-Moriya interaction. We believe that the present results will further stimulate research for materials containing transition metal ions with unusual valence states such as Fe^{5+} , which could lead to finding novel exotic properties and functionalities.

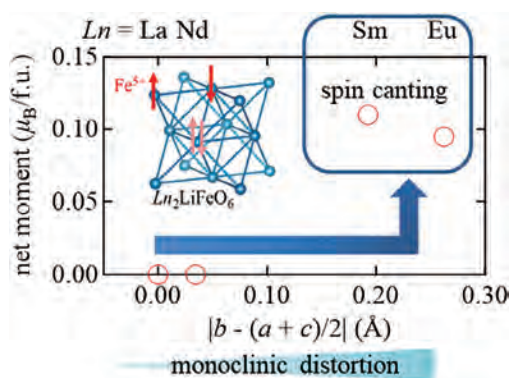


Figure 1. Net moment of $\text{Ln}_2\text{LiFeO}_6$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{and Eu}$) as a function of the magnitude of monoclinic distortion.

Electrochemical Control and Protonation of the Strontium Iron oxide SrFeO_y by Using Proton-Conducting Electrolyte

Utilizing electrochemical redox reactions and modulating transition metals' valence states enable one to electrically control structural and physical properties of transition metal oxides. Fabricating electric-field-effect transistor structures with gate insulators of electrolytes is a way for electrically inducing redox reactions in channels of oxide films and for electrochemically controlling oxides' physical properties.

In the work reported here, we used the proton-conducting solid electrolyte Nafion, which contains a large amount of water and protons, as a gate insulator and demonstrated electrochemical control and protonation of oxygen-deficient iron oxide SrFeO_y (SFO). Structural and electrical transport properties of SFO are known to depend on oxygen concentration y that ties with the Fe valence state (or the carrier density). When SFO is oxidized and y is close to 3, the oxygenated SFO (SrFeO_3) containing Fe^{4+} exhibits metallic transport properties with low electrical resistivity. On the other hand, when oxygen vacancies are introduced and y is lowered to 2.5, SFO is transformed to the insulating brownmillerite $\text{SrFeO}_{2.5}$ containing only Fe^{3+} . Given that SFO is integrated as a channel layer in transistor structures having a gate insulator of Nafion, as shown in Figure 2, electrical properties of the SFO channels are expected to be controlled by electrochemical redox reactions. When a positive gate bias V_{GS} is applied, protons are injected into the channel, and the SFO layers would be electrochemically reduced. When a negative V_{GS} is applied, protons are removed from the channel, and the SFO layers are expected to be oxidized. In fact, as we expected, we show that fabricating transistor structures with Nafion as a gate insulator and applying electric-field redox reactions to SFO film channels enables nonvolatile and reversible control of channels' resistance. Furthermore, electrochemically reducing the channels is found to implant protons into SFO, leading to the formation of proton-accumulated oxide $\text{H}_x\text{SrFeO}_{2.5}$ that has not been seen so far.

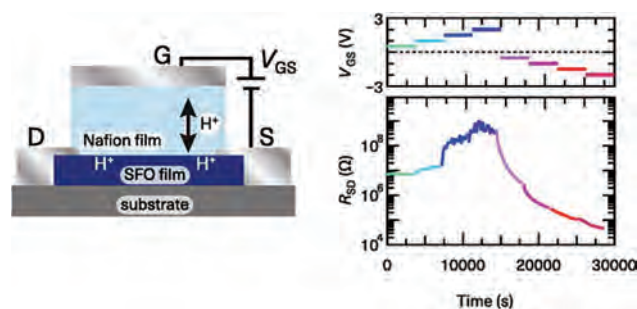


Figure 2. (left) Schematic illustration of electrochemical transistor device in which the proton-conducting solid electrolyte Nafion is used as a gate insulator. (right) Gate voltage V_{GS} dependence of the SrFeO_y channel resistance R_{SD} .