

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

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Prof
SHIMAKAWA, Yuichi
(D Sc)



Assoc Prof
KAN, Daisuke
(D Sc)



Assist Prof
SAITO, Takashi
(D Sc)



Techn Staff
ICHIKAWA, Noriya
(D Eng)



PD (JSPS)
AMANO PATINO,
Midori Estefani
(Ph D)



PD (JSPS)
HEO, Yooun
(Ph D)



PD
GOTO, Masato
(D Sc)



PD
GUO, Haichuan
(D Sc)

Students

XIONG, Peng (D3)
KOEDTRUAD, Anucha (D1)
TAN, Zhenhong (M2)
NIWA, Yasuyuki (M2)

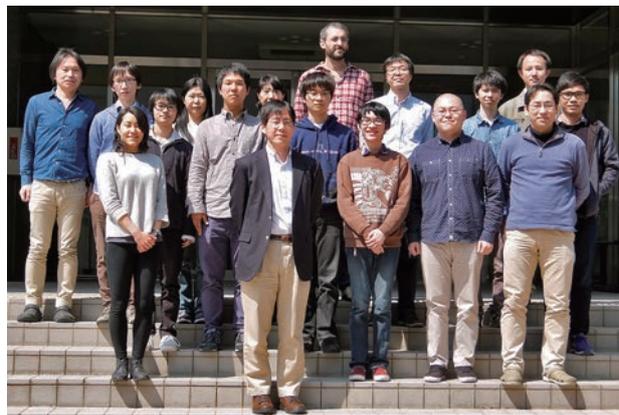
KOBAYASHI, Kento (M1)
SANTO, Junya (M1)
MATSUMOTO, Sho (M1)

KEYWORDS

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

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.



Selected Publications

Kan, D.; Aso, R.; Sato, R.; Haruta, M.; Kurata, H.; Shimakawa, Y., Tuning Magnetic Anisotropy by Interfacially Engineering the Oxygen Coordination Environment in a Transition-metal Oxide, *Nat. Mater.*, **15**, 432-437 (2016).
Chen, W.-T.; Mizumaki, M.; Seki, H.; Senn, M.; Saito, T.; Kan, D.; Attfield, J. P.; Shimakawa, Y., A Half-metallic A- and B-site-ordered Quadruple Perovskite Oxide $\text{CaCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12}$ with Large Magnetization and a High Transition Temperature, *Nat. Comm.*, **5**, 3909/1-7 (2014).
Matsumoto, K.; Haruta, M.; Kawai, M.; Sakaiguchi, A.; Ichikawa, N.; Kurata, H.; Shimakawa, Y., Selective Reduction of Layers at Low Temperature in Artificial Superlattice Thin Films, *Sci. Rep.*, **1**, 27/1-4 (2011).
Inoue, S.; Kawai, M.; Ichikawa, N.; Kageyama, H.; Paulus, W.; Shimakawa, Y., Anisotropic Oxygen Diffusion at Low Temperature in Perovskite-structure Iron Oxides, *Nat. Chem.*, **2**, 213-217 (2010).
Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y., Temperature-induced A-B Intersite Charge Transfer in an A-site-ordered $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ Perovskite, *Nature*, **458**, 60-63 (2009).

Charge and Spin Order in $\text{Ca}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$

Unusually high-valent transition-metal ions in ABO_3 perovskite-related oxides have been the subject of significant attention due to the rich variety of physical properties they can display. These materials are of particular interest as their inherent electronic instabilities are often relieved via charge disproportionation (CD). The perovskite $\text{Ca}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ has recently been reported to contain unusually high-valent $\text{Fe}^{3.5+}$ and to undergo sequential charge transitions on cooling. Magnetic and transport properties show significant anomalies associated with the charge transitions. In this study we present detailed analysis of the crystal and magnetic structures of this material with neutron powder diffraction data and reveal that $\text{Ca}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ undergoes a remarkable sequence of CD and charge-transfer (CT) transitions on cooling due to competing electronic instabilities: $\text{Ca}_{0.5}\text{Bi}_{0.5}^{3+}\text{Fe}^{3.5+}\text{O}_3 \rightarrow \text{Ca}_{0.5}\text{Bi}_{0.5}^{3+}\text{Fe}_{0.67}^{3+}\text{Fe}_{0.33}^{4.5+}\text{O}_3$ (CD phase) $\rightarrow \text{Ca}_{0.5}\text{Bi}_{0.25}^{3+}\text{Bi}_{0.25}^{5+}\text{Fe}^{3+}\text{O}_3$ (CT phase). As shown in Figure 1, the CT phase adopts a simple G-type antiferromagnetic structure of Fe^{3+} spins but the CD phase adopts an unusual charge and magnetic arrangement in which Fe^{3+} spins are antiferromagnetically ordered but the $\text{Fe}^{4.5+}$ moments have no long-range order due to magnetic frustration and form a spin glass at low temperatures.

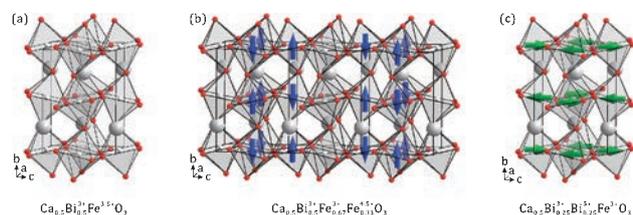


Figure 1. Refined structures of the three phases of $\text{Ca}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ showing the Fe spin orders in the low-temperature CD (middle) and CT phases (right).

Melting of Oxygen Vacancy Order at Oxide–Heterostructure Interface

Modifications in oxygen coordination environments in heterostructures consisting of dissimilar oxides often emerge and lead to unusual properties of the constituent materials. Engineering the oxygen coordination environments at the heterostructure interfaces is thus considered a

new way of tailoring functional properties. Although lots of attention has been paid to slight modifications in the rigid oxygen octahedra of perovskite-based heterointerfaces, revealing the modification behaviors of the oxygen coordination environments in the heterostructures containing oxides with oxygen vacancies have been challenging. Here, we performed cross-sectional HAADF- and ABF-STEM observations for heterointerface between $\text{SrFeO}_{2.5}$ (SFO) and DyScO_3 (DSO), and found that a significant modification in the oxygen coordination environments -melting of oxygen vacancy order- is induced at the SFO/DSO heterointerface. When an oxygen-deficient perovskite (brownmillerite structure) $\text{SrFeO}_{2.5}$ film grows epitaxially on a perovskite DyScO_3 substrate, both FeO_6 octahedra and FeO_4 tetrahedra in the (101)-oriented $\text{SrFeO}_{2.5}$ thin film connect to ScO_6 octahedra in DyScO_3 . As a consequence of accommodating a structural mismatch, the alternately ordered arrangement of oxygen vacancies is significantly disturbed and reconstructed in the 2 nm thick heterointerface region (Figure 2). The stabilized heterointerface structure consists of Fe^{3+} octahedra with an oxygen vacancy disorder. The melting of the oxygen vacancy order, which in bulk $\text{SrFeO}_{2.5}$ occurs at 1103 K, is induced at the present heterointerface at ambient temperatures.

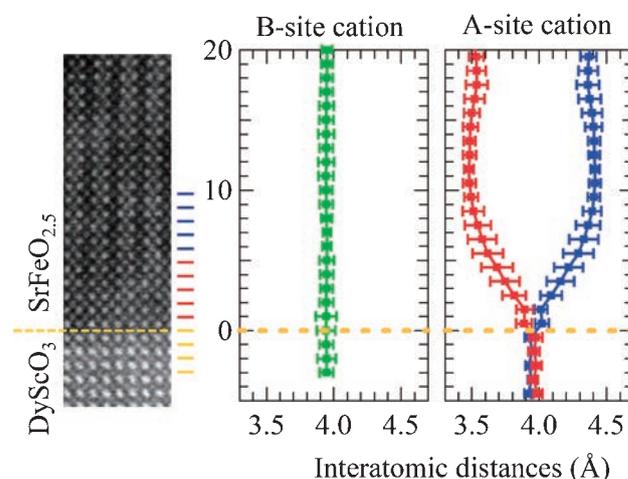


Figure 2. Cross-sectional HAADF-STEM image of the SFO/DSO heterostructure. In-plane interatomic distances of B-site (Fe or Sc) cations and A-site (Sr or Dy) cations across the interface as a function of the atomic position along the out-of-plane direction of the film. The topmost ScO_2 layer in DyScO_3 is defined as the zeroth atomic row (dashed yellow lines)