

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

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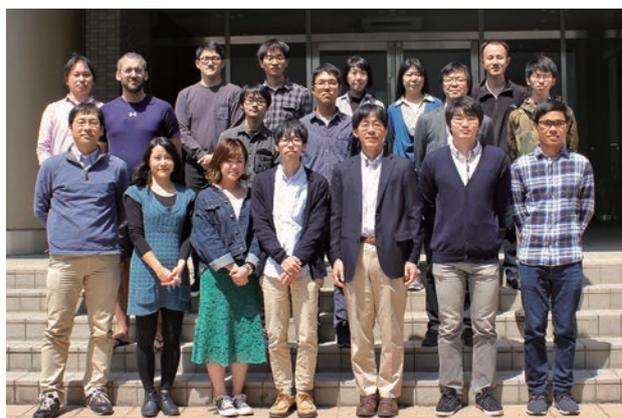
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KEYWORDS

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

Denis Romero, F.; Xiong, P.; Amano Patino, M.; Saito, T.; Kayser, P.; Attfield, J. P.; Shimakawa, Y., Suppression of Sequential Charge Transitions in $\text{Ca}_{0.5}\text{Bi}_{0.5}\text{FeO}_3$ via B-Site Cobalt Substitution, *Chem. Mater.*, **30**, 5493-5499 (2018).
Tan, Z.; Saito, T.; Denis Romero, F.; Amano Patino, M.; Goto, M.; Chen, W.-T.; Chuang, Y.-C.; Sheu, H.-S.; Shimakawa, Y., Hexagonal Perovskite $\text{Ba}_4\text{Fe}_3\text{NiO}_{12}$ Containing Tetravalent Fe and Ni Ions, *Inorg. Chem.*, **57**, 10410-10415 (2018).
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]-[3909-7] (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]-[27-4] (2011).

Hexagonal Perovskite $\text{Ba}_4\text{Fe}_3\text{NiO}_{12}$ Containing Tetravalent Fe and Ni Ions

Some 3d-transition-metal ions in oxides can show unusually high valence states, in addition to the conventional valence states. It has been reported that both unusually high valence Fe^{4+} and Ni^{4+} are stabilized in hexagonal-type perovskite structure oxides, whose chemical formula is ABO_3 . Fe^{4+} in BaFeO_3 (BFO) is stabilized with the 6H hexagonal perovskite structure, while unusually high valence Ni^{4+} is stabilized in the 2H hexagonal perovskite BaNiO_3 (BNO).

In this study, we synthesized $\text{Ba}(\text{Fe}_x\text{Ni}_{1-x})\text{O}_3$ with end members of BaNiO_3 ($x = 0$) and BaFeO_3 ($x = 1$), and investigated their crystal structures and magnetic properties. We successfully synthesized by a high-pressure and high-temperature technique a new single phase, $\text{Ba}_4\text{Fe}_3\text{NiO}_{12}$ ($x = 0.75$), that adopts the 12R perovskite structure with the space group $R\bar{3}m$. Mössbauer spectroscopy results and structure analysis using synchrotron and neutron powder diffraction data revealed that Fe^{3+} occupies the corner-sharing octahedral site while the unusually high valence Fe^{4+} and Ni^{4+} occupy the face-sharing octahedral sites in the trimers, giving a charge formula of $\text{Ba}_4\text{Fe}^3\text{Fe}^{4+}_2\text{Ni}^{4+}\text{O}_{11.5}$. At temperatures below about 200 K, this compound shows a ferromagnetic-like behavior with small magnetization. Ni^{4+} is suggested to have a low-spin electron configuration and not contribute to the magnetic properties of the compound, and thus, the observed weak ferromagnetism of this compound seems to originate from ferrimagnetic coupling between Fe^{3+} and Fe^{4+} spins.

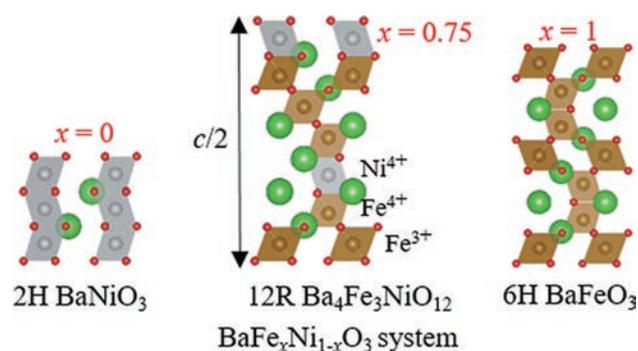


Figure 1. Crystal structures of 2H BaNiO_3 (left), 12R $\text{Ba}_4\text{Fe}_3\text{NiO}_{12}$ (middle) and 6H BaFeO_3 (right).

Nanoscale Oxygen Ion Dynamics in $\text{SrFeO}_{2.5+\delta}$ Epitaxial Thin Films

A variety of functional properties in transition metal oxides are often underpinned by oxygen vacancies. While the oxygen vacancy concentration and arrangements are well-known to have strong influence on physical properties of oxides, the oxygen dynamics in oxides—including oxygen ion incorporation and movements during redox reactions—remain elusive. Oxygen deficient iron-based perovskite-structured oxides $\text{SrFeO}_{2.5+\delta}$ ($0 \leq \delta \leq 0.5$) exhibit electrical transport properties that are closely associated with the oxygen off-stoichiometry. This conducting property in $\text{SrFeO}_{2.5+\delta}$ thus allows one to evaluate oxygen dynamics involving local redox reactions. In this study, by using combinations of X-ray diffraction (XRD) and conducting AFM (c-AFM), we characterize structures and local conduction properties associated with redox reactions in $\text{SrFeO}_{2.5+\delta}$ epitaxial thin films and evaluate nanoscale oxygen dynamics. Our c-AFM observations reveal that brownmillerite-to-perovskite structural changes due to air-annealing and oxidizing the film enhances conduction only in the terraces near the outer step edges. This indicates that the oxidation proceeds by preferential incorporation of oxygen in the local regions of the terraces and by diffusion of the incorporated oxygen into the film. We also show that the local conduction in the film can be controlled by electric-field-induced redox reactions. Our results highlight the significance of nanoscale oxygen dynamics and associated redox reactions in $\text{SrFeO}_{2.5}$ films.

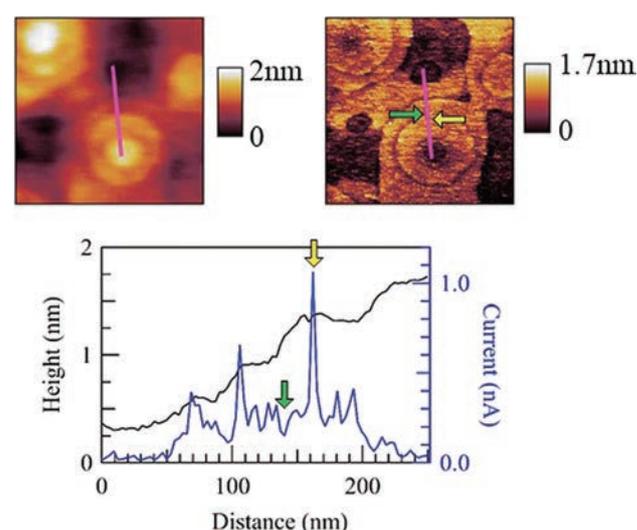


Figure 2. High-resolution topography and c-AFM images of the $\text{SrFeO}_{2.5+\delta}$ film. In the bottom, cross-section profiles along the pink lines in the topography and conduction images are plotted.