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

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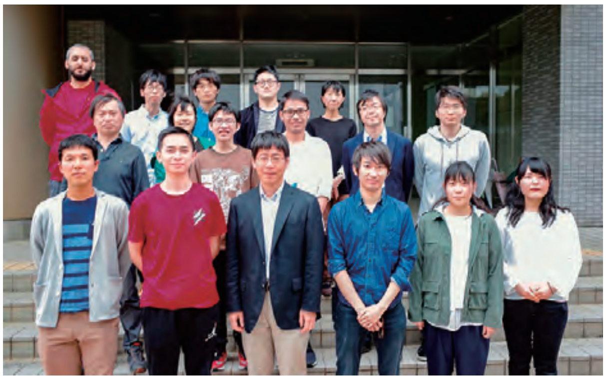
Scope of Research

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
Epitaxial Thin Film Growth
Functional Transition Metal Oxides
High Pressure Synthesis

Selected Publications

Denis Romero, F.; Shimakawa, Y., Charge Transitions in Perovskite Oxides Containing Unusually High-valent Fe, *Chem. Comm.*, **55,** 3690-3696 (2019).

Goto, M.; Saito, S.; Shimakawa, Y., Unusual Ferromagnetic Metal: A-Site-Layer-Ordered Double Perovskite YBaCo$_2$O$_6$ with Unusually High Valence Co$^{3.5+}$, *Chem. Mater.*, **30,** 8702-8706 (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 CaCu$_3$Fe$_2$Re$_2$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).

Unusual Ferromagnetic Metal: A-site-Layer-Ordered Double Perovskite $YBaCo_2O_6$ with Unusually High Valence $Co^{3.5+}$

A-site cation order in the double perovskites is much less common than B-cation order and a few compounds with the A-site-layered order were reported. Among them, layer-ordered oxygen-deficient perovskites, $RBaCo_2O_5$ (R: Y or lanthanoid) with mixed-valence $Co^{2.5+}$, are structurally interesting compounds. The layer ordering of R^{3+} and Ba^{2+} induces the layer ordering of oxygen vacancies along the stacking direction, giving an apically connected double layer of corner-sharing CoO_5 square pyramids (Figure 1). In this class of compounds, extra oxygen δ can be introduced into the R-layer, changing them into $RBaCo_2O_{5+\delta}$ with CoO_5 pyramids and CoO_6 octahedra. The extra oxygen δ not only modifies the local oxygen coordination but also increases the valence state of the Co ions. As a result, the electronic structures of the compounds and spin states of the Co ions are significantly changed, giving rise to a wide variety of physical properties

In this study, we have synthesized a fully oxygenated polycrystalline sample of $YBaCo_2O_6$ by low-temperature topochemical ozone oxidation of the precursor $YBaCo_2O_5$ (Figure 1). Structure analysis with synchrotron X-ray diffraction data revealed that $YBaCo_2O_6$ crystallizes in a tetragonal structure at room temperature and shows an orthorhombic distortion below approximately 140 K. At the structural transition temperature, a ferromagnetic transition is induced, which suggests strong spin-lattice coupling. $YBaCo_2O_6$ contains unusual high valence $Co^{3.5+}$ and the spins order ferromagnetically below 140 K. Low temperature electronic heat capacity data revealed that the compound is a metal with strong electronic correlation. The DFT calculation clarified that the up-spin band mainly contributes the metallic property in the spin polarized electronic structure. Therefore, the present A-site-layer-ordered double perovskite $YBaCo_2O_6$ with unusual high valence $Co^{3.5+}$ is concluded to be an unusual ferromagnetic metal with strong electron correlation.

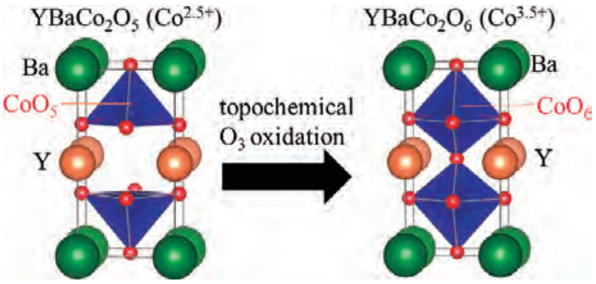


Figure 1. Crystal structures of $YBaCo_2O_5$ and $YBaCo_2O_6$.

Selective Growth of α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4 at Low Temperatures and Under Ambient Pressure

Various functional properties for transition metal oxides are closely tied to the oxides' structural phases and the valence states of the constituent transition metals. Engineering crystal structures and cations' valence states is therefore a key for exploring functional properties, and developing techniques for such engineering has been one of the central issues in materials science research. In this study, we utilized mist chemical vapor deposition (mist CVD), in which ultrasonically atomized chemical solutions of precursors are used as starting materials and are transferred to the substrate surface under ambient conditions, enabling ones to (epitaxially) grow polymorphs of various binary oxides at relatively low temperatures.

Our focuses are on binary iron oxides which are well-known to have various structural phases and to accommodate +2 and +3 valence states of Fe. Here we show that that using mist CVD to synthesize iron oxides at relatively low temperatures (~400 °C) and under ambient (non-vacuum) conditions enables their crystal structures and Fe valence states (hematite, maghemite and magnetite) to be selectively controlled (Figure 2). We found that the structural phases (polymorphs) and preferred orientation of the iron oxides are strongly influenced by the surface structure of the substrate, while the valence states of Fe depend on the solvent in which the Fe precursor is dissolved (water or methanol). α-Fe_2O_3 and γ- Fe_2O_3 films, both of which contain iron that is in only its +3 valence state, are grown by atomizing the aqueous solution of the Fe precursor and transferring them to the (001) Al_2O_3 and (001) $SrTiO_3$ substrates. On the other hand, Fe_3O_4 films in which Fe^{3+} and Fe^{2+} coexist were grown from the mist made from the alcoholic solution. We also show that the fabricated films exhibit distinct magnetic properties depending on their crystal structures and the Fe valence states.

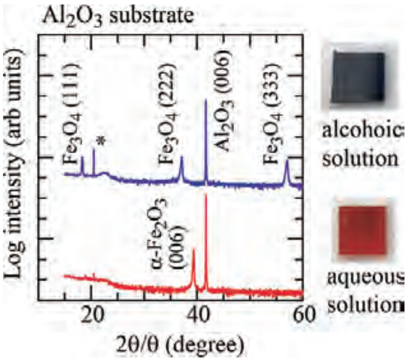


Figure 2. Photographs and X-ray 2θ/θ profiles for (upper) Fe_3O_4 and (lower) α-Fe_2O_3 films grown on (001) Al_2O_3 substrates.