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

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Scope of Research

Transition metal oxides display a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides have been 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. With advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth, we are currently exploring such functional oxides.

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

Selected Publications

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 $CaCu_3Fe_2Re_2O_{12}$ with Large Magnetization and a High Transition Temperature, *Nature 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. Reprts*, **1,** [27-1]-[27-4] (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 $LaCu_3Fe_4O_{12}$ Perovskite, *Nature*, **458,** 60-63 (2009).

A Half-metallic A- and B-site-ordered Quadruple Perovskite Oxide $CaCu_3Fe_2Re_2O_{12}$ with Large Magnetization and a High Transition Temperature

Materials with spin-polarized conduction electrons are of considerable interest in magnetic and electronic materials' research and for technological applications such as spin-polarized field emission and spin-polarized tunneling devices. Transition metal oxides with an ordered double-perovskite structure $A_2BB'O_6$, where the transition metal ions B and B´ are arranged alternately in a rock-salt manner, are useful materials for spintronic applications. An important example is Sr_2FeMoO_6, which is half-metallic and shows substantial TMR at room temperature. The B-site Fe^{3+} ($3d^5$, S=5/2) and the B´-site Mo^{5+} ($4d^1$, S=1/2) spins couple antiferromagnetically, leading to ferrimagnetism.

In this study, we have explored a strategy for enhancing spintronic properties relative to double perovskites by introducing further magnetic cations that can participate in a 1:3 order at the A sites, leading to the discovery of a new A- and B-site ordered quadruple perovskite oxide with large magnetization and a high magnetic ordering temperature. We have successfully synthesized a new A- and B-site-ordered quadruple perovskite oxide, $CaCu_3Fe_2Re_2O_{12}$ (Figure 1) by a solid-state reaction at a high temperature (1400 K) and high pressure (10 GPa). The magnetic and transport property measurements and electronic structure calculation reveal that the material has spin-polarized conduction electrons and is ferrimagnetic up to 560 K. The couplings between the three magnetic cations lead to the high Curie temperature, a large saturation magnetization of 8.7 μ_B and a half-metallic electronic structure, in which only minority-spin bands cross the Fermi level, producing highly spin-polarized conduction electrons. Spin polarization is confirmed by an observed low-field magnetoresistance effect in a polycrystalline sample. Optimization of $CaCu_3Fe_2Re_2O_{12}$ and related quadruple perovskite phases is expected to produce a new family of useful spintronic materials.

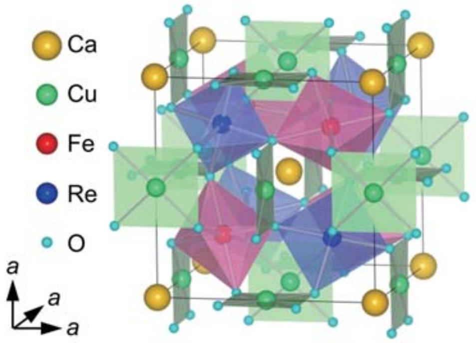

Figure 1. Crystal structure of A- and B-site ordered quadruple perovskite oxide $CaCu_3Fe_2Re_2O_{12}$.

Low-temperature Reduction in Oxide Heterostructures

Transition-metal ions in oxides can modify their oxidation states and oxygen coordinations. In iron oxides like $CaFeO_x$ the oxidation state of the Fe ions in the perovskite-structure framework changes from Fe^{2+} to Fe^{4+} when the oxygen content x changes from 2 to 3. Because oxygen ions are incorporated into and released from the perovskite structure framework during oxidation and reduction reactions, tracking structural phase associated with the change in the oxygen contents provides us an excellent platform to see oxygen-ion migration in the oxides.

Given that a topotactic reaction between $CaFeO_2$ (CFO2) and $CaFeO_{2.5}$ (CFO2.5) takes place at low temperatures below 300 °C, the low-temperature reduction and oxidation of artificial oxide heterostructures would provide us interesting information on oxygen-ion migrations. In this study we have investigated low-temperature reduction of $LaAlO_3$(LAO)/CFO2.5 heterostructures made on $SrTiO_3$ substrates by pulsed laser deposition. We found that the CFO2.5 layer in the heterostructures were reduced to a layer of CFO2 with an infinite-layer by the low-temperature CaH_2 treatment while the structure of the LAO layer remains unchanged. A key observation is that the time needed to reduce the CFO2.5 in the heterostructures to CFO2 depended on the lattice matching of the capping layer LAO to the CFO2.5 one (Figure 2). This suggests that the oxygen ions migrate through the coherently-grown strained LAO layer of the heterostructures predominantly in the out-of-plane direction and that the kinetics of the oxygen-ion migration is determined by the LAO/CFO2.5 interface. The present experimental results revealed the importance of lattice relaxation at the interface in the oxide heterostructure with regard to oxygen-ion migration behavior.

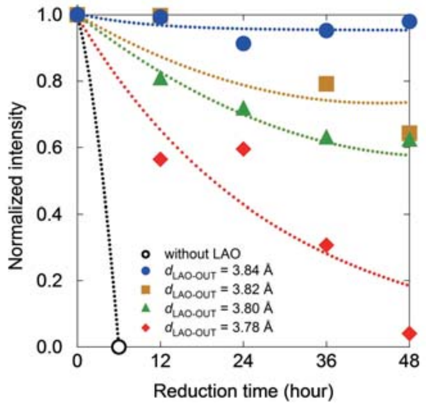

Figure 2. CFO2.5 (080) x-ray diffraction intensity as a function of reduction time for the LAO/CFO2.5 heterostructures with different lattices of the LAO capping layer. The plotted intensities are normalized by the intensity for the as-prepared heterostructure. The result without a capping layer (black) is also plotted for comparison.