

# International Research Center for Elements Science - Advanced Solid State Chemistry -

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Northwestern University, USA, 26 May 2009

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## Scope of Research

Transition-metal oxides show lots of interesting and useful properties. They include ferroelectrics, ferromagnets, conductors, batteries, and so on. These materials are widely used in current electronic devices. The wide variety of their crystal structures gives rise to various electronic structures, which lead to interesting and useful physical and chemical properties. We are focusing on the fundamental physics and chemistry of these “functional oxides” and seeking new materials with new functions. We are conducting systematic studies of material synthesis based on phase equilibrium information. Precise crystal structures are analyzed by X-ray and neutron diffractions. Electronic and magnetic structures are discussed based on the results of electronic structure calculations and physical property measurements.

## Research Activities (Year 2009)

### Publications

Long YW, 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).

Kawai M, Ito K, Shimakawa Y: Resistance Switching in a Single-crystalline NiO Thin Film Grown on a  $\text{Pt}_{0.8}\text{Ir}_{0.2}$  Electrode, *Applied Physics Letters*, **95**, [012109-1]-[012109-3] (2009).

### Presentations

New Perovskite-type Structure Oxides: High-pressure Synthesized Bulks and Epitaxially Grown Thin Films: Shimakawa Y, Gordon Research Conferences, Solid State Chemistry, Oxford, UK, 2 September 2009.

Ferromagnetic Cuprates  $\text{CaCu}_3\text{B}_4\text{O}_{12}$  ( $B = \text{Ge, Sn}$ ) Synthesized under High Pressure: Saito T, International Conference on High Pressure Science and Technology, Tokyo, Japan, 31 July 2009.

Frustrated  $S=3/2$  Honeycomb Antiferromagnet  $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ : Azuma M, International Conference on Magnetism, Superconductivity and Phase Transitions in Novel and Complex Materials 2009, Kolkata, India, 12 November 2009.

### Grant

Shimakawa Y, Strategic State-of-the-art Solid State Chemistry for New Functional Materials: Exploring for New Multi-functional Materials, Creative Scientific Research, 1 April 2007–31 March 2012.

## Temperature-Induced A–B Intersite Charge Transfer in an A-Site-Ordered LaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub> Perovskite

Changes of valence states in transition-metal oxides often cause significant changes in their structural and physical properties. Chemical doping is the conventional way of modulating these valence states. In ABO<sub>3</sub> perovskite and/or perovskite-like oxides, chemical doping at the A site can introduce holes or electrons at the B site, giving rise to exotic physical properties like high-*T<sub>c</sub>* superconductivity and colossal magnetoresistance. When valence-variable transition metals at two different atomic sites are involved simultaneously, we expect to be able to induce charge transfer -and, hence, valence changes- by using a small external stimulus rather than by introducing a doping element. Materials showing this type of charge transfer are very rare, however, and such externally induced valence changes have been observed only under extreme conditions like high pressure. We found unusual temperature-induced valence changes at the A and B sites in the A-site-ordered double perovskite LaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub> (Figure 1); the underlying intersite charge transfer is accompanied by considerable changes in the material's structural, magnetic and transport properties. When cooled, the compound shows a first-order, reversible transition at 393K from LaCu<sup>2+</sup><sub>3</sub>Fe<sup>3.75+</sup><sub>4</sub>O<sub>12</sub> with Fe<sup>3.75+</sup> ions at the B site to LaCu<sup>3+</sup><sub>3</sub>Fe<sup>3+</sup><sub>4</sub>O<sub>12</sub> with rare Cu<sup>3+</sup> ions at the A site. Intersite charge transfer between the A-site Cu and B-site Fe ions leads to paramagnetism-to-antiferromagnetism and metal-to-insulator isostructural phase transitions. What is more interesting in relation to technological applications is that this above-room-temperature transition is associated with a large negative thermal expansion.

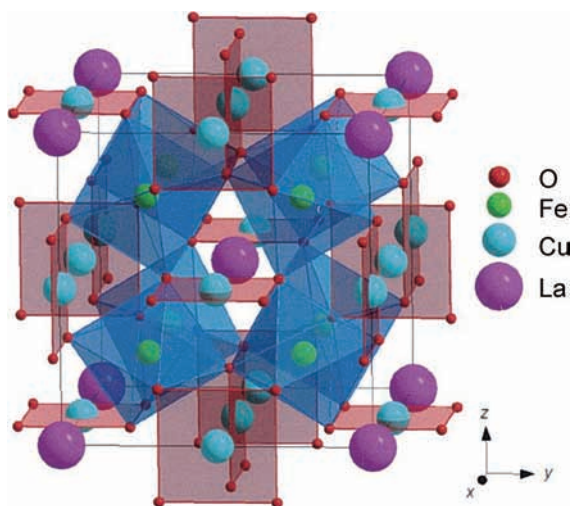


Figure 1. Crystal structure of LaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub>

## Resistance Switching in a Single-Crystalline NiO Thin Film Grown on a Pt<sub>0.8</sub>Ir<sub>0.2</sub> Electrode

Resistance switching (RS) phenomena in an M/NiO/M (M: Metal) capacitor structure, where a thin film of NiO is sandwiched between two metal electrode layers, have attracted much attention because of their potential applications for resistive random access memories. The RS in a polycrystalline NiO thin film has been explained by a filamentary conducting path mechanism, in which formation and rupture of the conducting filaments in the oxide layer. However, the properties also affected by grain and/or domain boundaries in the polycrystalline sample. In order to see the “intrinsic” behaviors of filaments, investigations of RS properties in a single-crystalline NiO thin film are needed. We recently succeeded in preparing Pt/NiO/Pt-Ir with a single-crystalline NiO thin film on an atomically flat Pt-Ir epitaxial bottom electrode layer (Figure 2). The memory cells showed unipolar resistance switching behaviors (Figure 3). The result demonstrates that unipolar resistance switching is not a characteristic phenomenon in the polycrystalline NiO but it can also occur in the single-crystalline NiO.

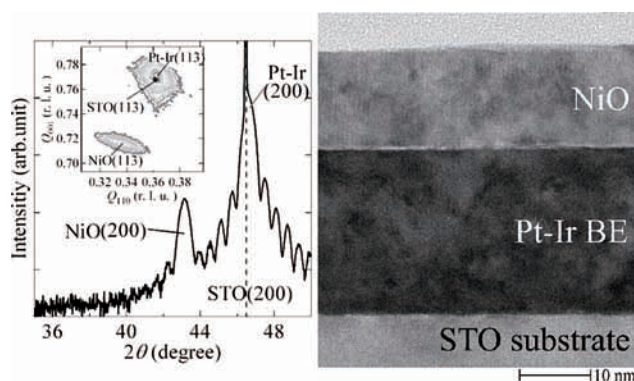


Figure 2. X-ray diffraction profiles and a cross-sectional TEM image of a Pt/NiO/Pt-Ir capacitor structure.

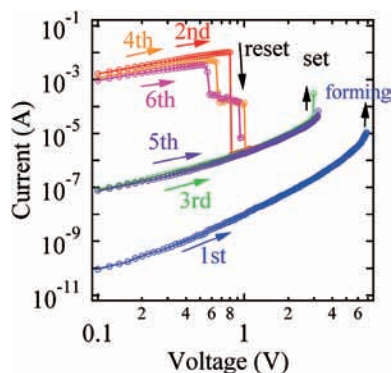


Figure 3. RS behaviors observed in an Pt/NiO/Pt-Ir capacitor.