

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

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Assoc Prof VALANOOR, Nagarajan	University of New South Wales, Australia, 22 January
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Prof WILEY, John B.	University of New Orleans, USA, 1 March
Prof ATTFIELD, J. Paul	University of Edinburgh, UK, 15 March
Prof PAULUS, Werner	University of Rennes 1, France, 25 March
Prof LOYE, Hans-Conradzur	University of South Carolina, USA, 24 May
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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	High Pressure Synthesis
Functional Transition Metal Oxides	Perovskite Structure
Epitaxial Thin Film Growth	



Selected Publications

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 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).

Anisotropic Oxygen Diffusion at Low Temperature in Perovskite Structure Iron Oxides

Oxygen-ion conduction in transition-metal oxides has been extensively investigated due to its potential of device applications such as electrolytes in solid-oxide fuel cells and oxygen-separation membranes. However the operation temperature is currently limited to only high temperature region. Achieving enough oxygen ion conduction at lower temperature is, therefore a key to further developments of the oxygen-ion conduction based devices. Furthermore an understanding of the oxygen-diffusion pathways in the oxides would provide ideas on ideal structures that allow the efficient ion conduction at lower temperatures.

Here we report that brownmillerite-structured $\text{CaFeO}_{2.5}$ epitaxial thin films undergo a structural change into CaFeO_2 with an infinite-layer structure (Figure 1) through low-temperature reductions with CaH_2 .

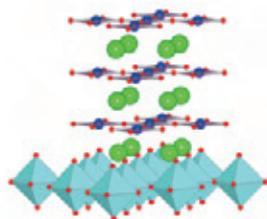


Figure 1. Schematic infinite-layer structure CaFeO_2 on a substrate.

We found that some of the oxygen atoms are released from the perovskite-structure framework and others are rearranged within it during the reduction process. Both the observed structural changes and the reaction time necessary for the reduction process on the film orientations show the strong dependence on the film orientations. This reveals two oxygen diffusion pathways and the related kinetics at low temperature. These results demonstrate that oxygen diffusion in the brownmillerite is highly anisotropic, significantly higher along the lateral direction of the tetrahedral and octahedral layers as shown in Figure 2.

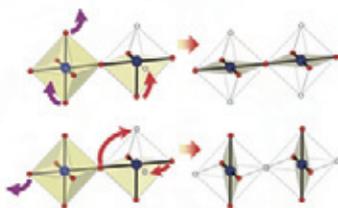


Figure 2. Schematics of two types of oxygen diffusion pathways and the rearrangement from tetrahedral to square-planar coordination in FeO_4 .

Charge Transfer and Antiferromagnetic Order in The A-site-ordered Perovskite $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$

A-site-ordered double perovskite oxides with the general formula $\text{AA}'_3\text{B}_4\text{O}_{12}$ have attracted enormous interest owing to their wide variety of physical properties. Recently we found a novel A-site-ordered double perovskite oxides $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ displaying a temperature-induced intersite charge transfer. This charge transfer is attributed to the simultaneous valence changes between the A' and B sites, namely $3\text{Cu}^{2+} + 4\text{Fe}^{3.75+} \rightarrow 3\text{Cu}^{3+} + 4\text{Fe}^{3+}$ where the paramagnetic metallic phase at higher temperature transforms to the antiferromagnetically-ordered insulating phase at lower temperature. In this study we employed high resolution neutron powder diffraction to investigate the charge states and spin order in this compound. We found that a first-order phase transition takes place at $T_{\text{CT}} \sim 400$ K between cubic $Im\bar{3}$ structures with charge distributions $\text{LaCu}^{3+}_3\text{Fe}^{3+}_4\text{O}_{12}$ and $\text{LaCu}^{2+}_3\text{Fe}^{3.75+}_4\text{O}_{12}$. Bond valence sums confirm that these charge states are adopted in the two phases, and there are no substantial valence fluctuations near the charge transfer transition. G-type antiferromagnetic order of Fe^{3+} spins at the B-site is observed in the low temperature phase $\text{LaCu}^{3+}_3\text{Fe}^{3+}_4\text{O}_{12}$ and the ordered moment at 50 K is $4.0 \mu_B$. Magnetic moment is absent at the A'-site Cu^{3+} cation. The thermal evolution of the ordered moment enables an intrinsic $T_N \sim 600$ K to be estimated, although the actual upper limit for the spin order is T_{CT} (Figure 3). No long range magnetic ordering is also found in the high temperature phase, $\text{LaCu}^{2+}_3\text{Fe}^{3.75+}_4\text{O}_{12}$, showing that any ordering transition for this regime has $T_M < T_{\text{CT}}$.

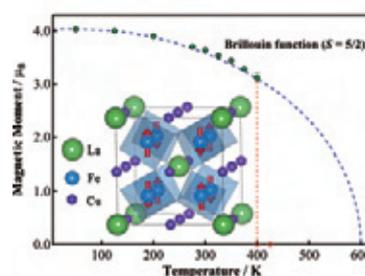


Figure 3. Temperature dependence of the refined Fe^{3+} magnetic moment at the B-site in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. The inset shows the crystal structure of the low temperature phase with G-type antiferromagnetic ordering.