

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

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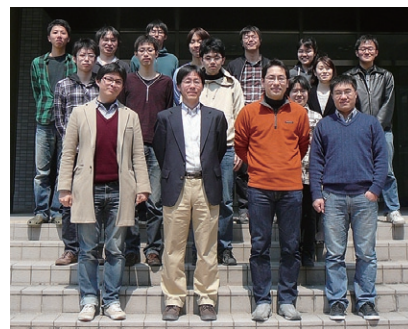
Prof GREEDAN, John. E.	McMaster University, Hamilton, Canada, 12 November
Prof SARMA, D. D.	Indian Institute of Science, India, 28 September
Prof YU, Jaejun	Seoul National University, Korea, 8 August
Prof POEPELMEIER, Ken	Northwestern University, U.S.A., 6 June
Prof LIU, Ru-Shi	National Taiwan University, Taiwan, 11–14 January
Prof ATTFIELD, J. Paul	University of Edinburgh, U.K., 11–14 January

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.; Saito, T.; Hayashi, N.; Takano, M.; Shimakawa, Y., Ligand-hole Localization in Oxides with Unusual Valence Fe, *Sci. Rep.*, **2**, 449/1-6 (2012).
Azuma, M.; Chen, W. T.; Seki, H.; Czapski, M.; Olga, S.; Oka, K.; Mizumaki, M.; Watanuki, T.; Ishimatsu, N.; Kawamura, N.; Ishiwata, S.; Tucker, M. G.; Shimakawa, Y.; Attfield, J. P., Colossal Negative Thermal Expansion in BiNiO₃ Induced by Intermetallic Charge Transfer, *Nat. Comm.*, **2**, 347 (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 LaCu₃Fe₄O₁₂ Perovskite, *Nature*, **458**, 60-63 (2009).
Kan, D.; Terashima, T.; Kanda, R.; Masuno, A.; Tanaka, K.; Chu, S.; Kan, H.; Ishizumi, A.; Kanemitsu, Y.; Shimakawa, Y.; Takano, M., Blue-light Emission at Room Temperature from Ar⁺-irradiated SrTiO₃, *Nat. Mater.*, **4**, 816-819 (2005).

Ligand-hole Localization in Oxides with Unusual Valence Fe

Unusual high-valence states of iron are stabilized in a few oxides. A-site-ordered perovskite-structure oxides (Figure 1) contain such iron cations and exhibit distinct electronic behaviors at low temperatures, e.g. charge disproportionation (CD) ($4\text{Fe}^{4+} \rightarrow 2\text{Fe}^{3+} + 2\text{Fe}^{5+}$) in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and intersite charge transfer (CT) ($3\text{Cu}^{2+} + 4\text{Fe}^{3.75+} \rightarrow 3\text{Cu}^{3+} + 4\text{Fe}^{3+}$) in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. We synthesized solid solutions of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, and revealed how the instabilities of high-valence state of Fe in the oxides are relieved from extensive investigations of structural, electronic and magnetic properties in the wide temperature ranges from 5 to 500 K.

In Figure 2 shown is a compositional phase diagram of the $(\text{Ca}_{1-x}\text{La}_x)\text{Cu}_3\text{Fe}_4\text{O}_{12}$ solid solution, which is derived from all the experimental results. We see that the CD and CT phases coexist in the intermediate compositions and that the intersite CT transition temperatures (T_{CT}) increase with increasing La doping (i.e., with increasing x), while the CD transition temperatures (T_{CD}) do not change from that of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$. To explain the behaviors, we proposed a model that localization of ligand holes which are produced by the strong hybridization of iron d and oxygen p orbitals, plays a significant role on the distinct electronic behaviors. In the proposed ligand-hole picture, CD behavior is regarded as charge ordering of the ligand holes ($4d^5\bar{L} \rightarrow 2d^5 + 2d^5\bar{L}^2$). On the other hand, CT is regarded as a Mott transition of the ligand holes ($3d^9 + 4d^5\bar{L}^{0.75} \rightarrow 3d^9\bar{L} + 4d^5$). The difference between the CD and CT transitions is only the localization site of the ligand holes. This explains the coexistence of CT and CD in the solid solution. Our results demonstrate that the A-site-ordered perovskite-structure $\text{Ca}_{1-x}\text{La}_x\text{Cu}_3\text{Fe}_4\text{O}_{12}$ solid solution is a novel example exhibiting interplay of the interactions mediated by the ligand holes.

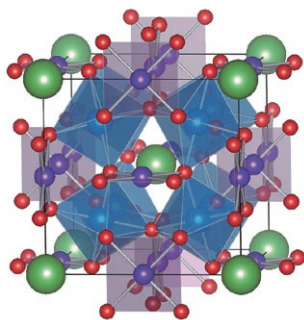


Figure 1. Crystal structure of the A-site-ordered double-perovskite.

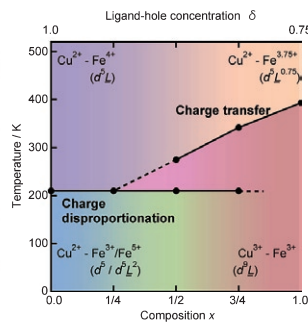


Figure 2. Compositional phase diagram for the $\text{Ca}_{1-x}\text{La}_x\text{Cu}_3\text{Fe}_4\text{O}_{12}$ solid-solution.

Thickness-Dependent Structure-Property Relationships in Strained (110) SrRuO_3 Thin Films

Recent advances in epitaxial thin films and heterostructures based on perovskite oxides have been some of the most exciting developments in functional materials. In particular, understanding of how the film accommodates epitaxial strain resulted from lattice mismatch between film and substrate is crucial as the strained films often show enhanced or modified functional properties as compared to the bulk counterpart. However, while it has been widely believed that the strain imposes new lattice constants on the film, what still remains unclear is how the perovskite lattice accommodates the increased elastic energy due to the epitaxial strain and how the strain accommodation affects physical properties of the film.

In this study, we investigated thickness-dependence of structure-property relationships in the strained SrRuO_3 (SRO) thin films. We found that, for the film thinner than 16 nm, the monoclinic structure with the $\sqrt{2}a_{\text{pc}} \times \sqrt{2}a_{\text{pc}} \times 2a_{\text{pc}}$ unit cell is epitaxially stabilized while the film thicker than 16 nm has the tetragonal structure with the cell-doubled $a_{\text{pc}} \times 2a_{\text{pc}} \times a_{\text{pc}}$ unit cell. The results of detailed structural characterizations indicate that the thickness-dependent structure change is ascribed to the substrate-induced modification in the RuO_6 octahedral rotation pattern in the strained film which has in-plane lattice parameters that are fixed by the substrate. We further demonstrate that physical properties are closely correlated with the film structure. The monoclinic film has the ferromagnetic transition temperature, T_c which increases up to 130 K with increasing the thickness while the tetragonal film has $T_c \sim 100$ K independent of the thickness. The magnetic anisotropy is also strongly affected by the film structures, indicating the importance of the magnetocrystalline effect in SRO. The results highlight that the epitaxial strain accommodation through the octahedral rotations in the strained SRO films plays a significant role in determining their structural phase and physical properties.

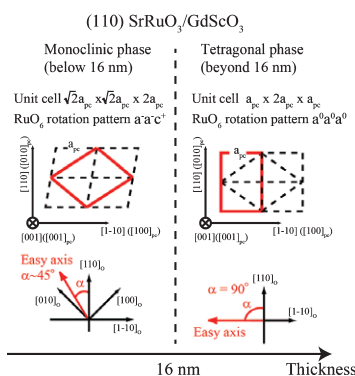


Figure 3. Thickness dependence of structure-property relationships in strained (110) SrRuO_3 thin films.