

Revealing the ligand-hole localization behaviors in oxides with unusual high-valence Fe

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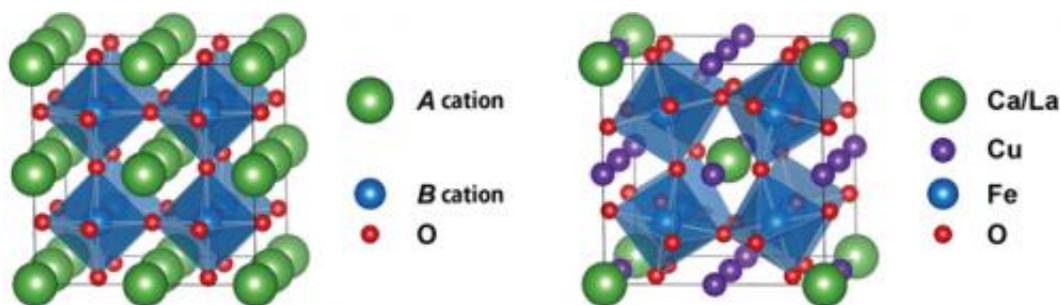


Fig. 1: Crystal structures of the simple perovskite ABO₃ (left) and the A-site-ordered double-perovskite AA'₃B₄O₁₂ (right).

Japanese researchers revealed the mechanism of the functional properties of oxides with unusual valence Fe. The paper was published in a Nature publishing group journal [Scientific Reports](#).

Iron ions in oxides usually show the +2 and +3 oxidation states typically seen in wüstite (Fe²⁺O), magnetite (Fe²⁺Fe³⁺2O₄), and hematite (Fe³⁺₂O₃). A few oxides, such as SrFeO₃ and CaFeO₃, contain unusual high-oxidation-state iron ions like Fe⁴⁺, and the behaviors of such high-valence iron ions have been attracting much attention for a long time.

The research team recently discovered new such compounds; CaCu₃Fe₄O₁₂ and LaCu₃Fe₄O₁₂ with the A-site-ordered perovskite

structure (see Fig. 1). The compounds contain iron ions with unusual valence states and exhibit distinct electronic behaviors at low temperatures, *e.g.* charge disproportionation ($4\text{Fe}^{4+} \rightarrow 2\text{Fe}^{3+} + 2\text{Fe}^{5+}$) in $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and intersite charge transfer ($3\text{Cu}^{2+} + 4\text{Fe}^{3.75+} \rightarrow 3\text{Cu}^{3+} + 4\text{Fe}^{3+}$) in $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$. In the present study, they made solid solutions of $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ and investigated their temperature-dependent transitions. Although the charge-disproportionation and intersite-charge-transfer behaviors look completely different from each other in simple ionic models, they can both be explained by the localization of ligand holes, which are produced by the strong hybridization of iron *d* and oxygen *p* orbitals in oxides. In the charge-disproportionated phase the ligand holes are localized at the Fe site and the transition is regarded as one to the rock-salt-type charge ordering of the ligand holes. In the intersite charge transfer, on the other hand, the ligand holes are localized at the Cu site and the transition can be regarded as a Mott transition of the ligand holes. *TCT* decreases with increasing concentration of the ligand-hole carriers (see Fig. 2).

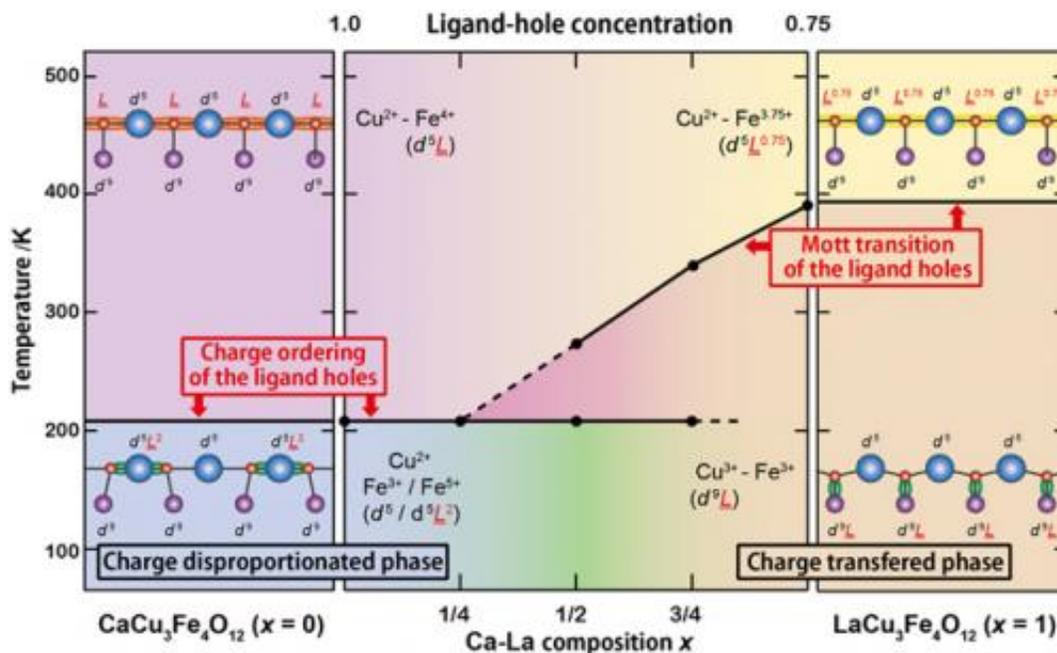


Fig. 2: Compositional phase diagram for the $\text{Ca}_{1-x}\text{La}_x\text{Cu}_3\text{Fe}_4\text{O}_{12}$ solid

solution and the ligand-hole localization model of charge disproportionation and intersite charge-transfer transition behaviors.

In the A-site-ordered perovskite-structure [oxides](#), transition metals at both A' and B sites mediate A'-A', A'-B, and B-B interactions that lead to intriguing physical properties. The ligand holes produced by the strong hybridization of transition-metal cation d orbitals and oxygen p orbitals also play important roles in giving rise to various electronic and structural properties. The present 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.

More information: Wei-Tin Chen, et al. Ligand-hole localization in oxides with unusual valence Fe. *Scientific Reports* 2, Article number: 449, 2012/06/11/online, [doi: 10.1038/srep00449](https://doi.org/10.1038/srep00449)

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