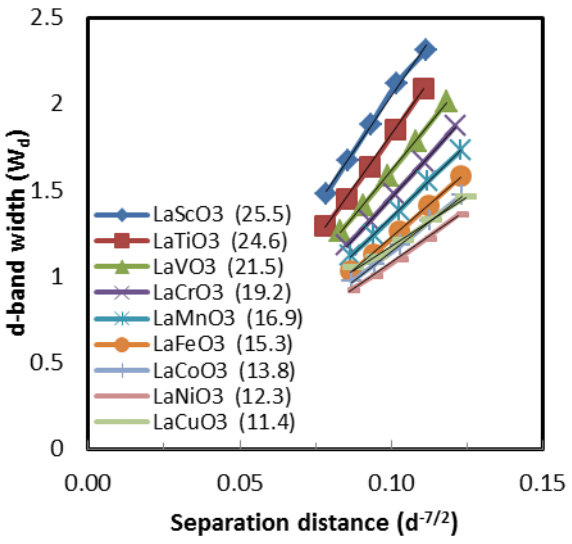
Designing the electronic structure and reactivity of metal oxides through strain, d-band filling and oxidation state

PIs: **John Kitchin,** Paul Salvador
Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

Metal oxides are used throughout catalysis as supports and active materials. Despite their ubiquity, it remains difficult to predict the reactivity of even model oxide surfaces. In stark contrast, there are well known correlations in metals and alloys for predicting their electronic structure and reactivity in terms of simple concepts such as strain, ligand effects and ensemble effects and the their effect on the electronic structure of the metals, particularly the d-band [1-3]. Effects of strain have been shown to be significant in oxide properties [4]. Oxides are notably more complex than metals; there are many more possible structures, oxides can tolerate nonstoichiometries in oxygen content that are simply not relevant in metals, and defect chemistry can dominate the electronic properties and reactivity in some cases. Nevertheless, the development of understanding in oxides analogous to that of metals is critical to enable the design of new materials at the nanoscale with desirable electronic structure and reactivity.

We have been developing a combined experimental/computational program to develop the understanding required to advance the design of new oxide materials with desired properties. We synthesize thin films (1-500 nm) of perovskites grown epitaxially on single crystal perovskite supports to introduce controlled amounts of strain into the thin film. We then utilize chemical reactivity probes to measure the effects of the strain on the reactivity of the thin films [5, 6]. In some cases we see a two order of magnitude increase in reactivity with strains of order 1%. In parallel, we are using density functional theory calculations to calculate the electronic structure and reactivity of perovskites. The figure shows how the d-band width of the B atom in the perovskite varies with strain, in accordance with a simple solid state physics-based model [7]. We are currently extending this work to develop models of perovskite reactivity that are analogous to those found in metals.



References

1. J.R. Kitchin, J.K. Nørskov, M.A. Barteau, and J.G. Chen, *Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces.* Physical Review Letters, 2004. **93**(15): p. 156801. (http://dx.doi.org/10.1103/PhysRevLett.93.156801)
2. J.R. Kitchin, J.K. Nørskov, M.A. Barteau, and J.G. Chen, *Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals.* The Journal of Chemical Physics, 2004. **120**(21): p. 10240-10246. (http://dx.doi.org/10.1063/1.1737365)

3. H. Xin and S. Linic, *Communications: Exceptions to the d-band model of chemisorption on metal surfaces: The dominant role of repulsion between adsorbate states and metal d-states.* The Journal of Chemical Physics, 2010. **132**(22): p. 221101-4. (http://dx.doi.org/10.1063/1.3437609)
4. A. Kushima, S. Yip, and B. Yildiz, *Competing strain effects in reactivity of $LaCoO_3$ with oxygen.* Physical Review B, 2010. **82**(11): p. 115435. (http://dx.doi.org/10.1103/PhysRevB.82.115435)
5. L. Yan, K.R. Balasubramaniam, S. Wang, H. Du, and P.A. Salvador, *Effects of crystallographic orientation on the oxygen exchange rate of $La_{0.7}Sr_{0.3}MnO_3$ thin films.* Solid State Ionics, 2011. **194**(1): p. 9-16. (http://dx.doi.org/10.1016/j.ssi.2011.05.004)
6. L. Yan, B. Kavaipatti, S. Wang, H. Du, and P. Salvador, *Electrical Conductivity Relaxation Study of Solid Oxide Fuel Cell Cathodes using Epitaxial (001)-Oriented Strontium-Doped Lanthanum Manganite Thin Films.* Mat. Res. Soc. Symp. Proc., 2010. **1255**(1255-M02-02).
7. S.A. Akhade and J.R. Kitchin, *Effects of strain, d-band filling, and oxidation state on the bulk electronic structure of cubic 3d perovskites.* J. Chemical Physics, 2011. **135**(10): p. 104702.