Thursday Morning, October 31, 2013

Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 202 B - Session MG+MI+NS-ThM

Theoretical and Computational Methods
Moderator: K. Cook-Chennault, Rutgers, the State University of New Jersey, L. Madsen, National Science Foundation (NSF)

8:40am MG+MI+NS-ThM3 Application of Computational Methods to Material Design and Discovery, *S.B. Sinnott*, University of Florida **INVITED**
Modeling of materials is an integral component in the design and discovery of materials as outlined in the Materials Genome Initiative. Illustrative examples are discussed where computational methods are used in conjunction with cutting-edge experimental methods. In the first example, electronic-structure, density functional theory calculations and empirical, atomic-scale simulations are used in conjunction with experimental synthesis and characterization to identify the features of Pt electrode/$PbTiO_3$ dielectric interfaces that lead to the degradation of devices. The results specify how the microstructure of the interface might be designed to improve performance. In the second example a combination of simple, electrostatic calculations, high-through-put experiments, and materials informatics is used to investigate the tribological properties of inorganic materials. The results are used to design a simple model to identify material properties that are indicative of solid-state lubrication. This work is supported by the National Science Foundation under grant DMR-1207293 and the Office of Naval Research

9:20am MG+MI+NS-ThM5 New Ferroelectrics and Antiferroelectrics by Design, *K.M. Rabe*, Rutgers, the State University of New Jersey **INVITED**
I will describe our work on the design and discovery of new classes of ferroelectric and antiferroelectric materials using a combined crystallographic database / first principles approach. For ferroelectrics, using the design principle that any polar structure type can have ferroelectric representatives if the barrier to switching is lowered by appropriate chemical variation, we have recently identified a new family of ferroelectrics in the intermetallic LiGaGe structure type. For antiferroelectrics, we used a design principle based on the close relationship between ferroelectrics and antiferroelectrics to identify a previously unrecognized class of antiferroelectrics, related to the LiGaGe-type ferroelectrics, in the MgSrSi structure type. The further development of design principles and their application will be discussed. The discovery of new classes of antiferroelectrics is expected to open the way to increased recognition and application of antiferroelectrics as functional materials.

10:40am MG+MI+NS-ThM9 Disruptive Design Strategies for Emergent Ferroics, *J.M. Rondinelli*, Drexel University
There are two main routes to accelerate materials discoveries for advanced electronic and sustainable energy technologies: serendipitous realization through conventional synthesis or computationally guided growth of novel materials through, *e.g.*, artificial structuring of bulk compounds at the atomic scale. Recently, the launch of the Materials Genome Initiative (MGI) at the national level has reinvigorated the search for new routes to accelerate the discovery of advanced materials for rapid deployment—the aim being to evolve a "hunter and gatherer" discovery paradigm into the cultivation of materials by design. This discovery process may be accelerated by merging applied theoretical crystallography, where the objective is transformed into (*i*) identifying suitable topologies – approximate geometric arrangements of structural building units – that lift particular symmetries, with electronic structure methods to (*ii*) search for microscopic mechanisms and external conditions that energetically stabilize those geometries. Such information may guide experimental explorations, whereby the synthetic efforts are focused on a more manageable (and largely reduced) structural data set by the theoretical (symmetry) considerations.

Here, we describe report an Ensemble Computation Materials Protocol (ECMP) with predictive capability to design and accelerate the discovery of a new class of *A*-site cation-ordered perovskite ferroelectrics from combinations of the centric, non-polar, transition metal–oxygen octahedra that form the perovskite framework. First, we describe the microscopic origin for the loss of inversion symmetry and the electric polarization in layered (*A,A'*)BO_3 perovskite oxides. We then show that the mechanism can

be translated to $A_nB_nO_{3n+1}$ (*n*=1,2) Ruddlesden-Popper (RP) oxides with disconnected layers of corner-sharing octahedra. We use the group theoretical methods to enumerate the structural criteria required to remove the mirror symmetry elements. Feasible chemistries are proposed using Bayesian inference methods. We then evaluate the stability of the possible ground state structures with density functional theory (DFT) calculations. We predict that ordering of divalent and trivalent cations in a layered RP manganite leads to a polar phase, space group $Pca2_1$, with a sizeable polarizations, which are supported by preliminary experimentsal. We anticipate that these findings and methodology will contribute to our understanding of not only new ferroic materials, but also that this general approach of physical properties by atomistic structure design within the MGI is immediately amenable to other material functionalities.

11:00am MG+MI+NS-ThM10 Computational Design of Materials for Catalysis: Interface Matters, *T.S. Rahman*, University of Central Florida **INVITED**
An important ingredient in computational design of functional materials is back and forth feedback between theory and experiment, which necessarily involves modeling of realistic environments, using accurate methods. In this talk, I will present results of our density functional theory based calculations which together with experimental observations help isolate catalyst descriptors for specific reactions, in particular for supported nanoparticles. For example, for methanol oxidation on Au nanoparticles on titania [1], the higher activity of interfacial sites can be traced to charge-transfer-induced Coulomb interaction among the gold, reactant, and reducible TiO2 support, brought about through the formation of an ionic O−Au bond between gold and methoxy in such sites, which turns the participating perimeter gold atom cationic. A direct result of such charge-transfer-induced repulsive interaction between cationic gold and positively charged C moiety of methoxy is activation of the positively charged C moiety of methoxy, as manifested by the pronounced elongation of O−C bond length and the tilting of the methoxy axis, which facilitate reaction of methoxy through C−H scission with the bridge oxygen atoms that are readily available from the reducible support. I will use the above guidelines to predict the reactivity of several titania supported metallic/bimetallic nanoparticles for oxidation of organic molecules with the structure of R−O−R', where R and R'are (saturated) hydrocarbons. Similarly, I will analyze the role of the interface (with the support) for a set of nanometer and sub-nanometer sized Pt nanoparticles on titania and alumina and point to the variations in the physical and chemical characteristics as a function of size, shape, and chemical environment (H and OH coverage). Through detailed comparison with XANES data [2], I will provide an understanding of the descriptors that control specific nanoparticle property.

[1] S. Hong and T. S. Rahman, J. Am. Chem. Soc., dx.doi.org/10.1021/ja4010738 (2013)

[2] F. Behafarid, L. K. Ono, S. Mostafa, J. R. Croy, G. Shafai, S. Hong, T. S. Rahman, Simon R. Bare and B. Roldan Cuenya, Phys. Chem. Chem. Phys., 2012, **14**, 11766–11779

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