INCORPORATING FINITE TEMPERATURE INTO MATERIALS BY DESIGN FOR NONSTOICHIOMETRIC COMPLEX FUNCTIONAL OXIDES

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Enabled by dramatic advancements in computational capabilities and the tightening integration of theory and experiment, materials by design is rapidly becoming a leading paradigm in materials science. However, to most effectively accelerate the pace of materials design and discovery, first-principles calculations must move closer to experimental reality by taking into account the finite temperature effects corresponding to typical growth and/or operating conditions. Our work aims to develop capabilities to incorporate these finite temperature effects, which include atomic and magnetic disorder as well as the temperature dependence of the free energies of solids, into modern materials by design.

We begin by integrating density functional theory (DFT) and experiment to investigate the properties of two nonstoichiometric complex functional oxides: $Sr_xLa_{1-x}Mn_yAl_{1-y}O_{3-\delta}$ (SLMA) and $BaCo_xFe_yZr_{1-x-y-z}Y_zO_{3-\delta}$ (BCFZY). SLMA has been demonstrated as a promising active material for high temperature (1000-1400 °C) solar thermochemical (STC) fuel production,[1] while BCFZY has been shown to allow simultaneous conduction of electronic charge carriers (holes), protons, and oxygen ions, enabling record-breaking protonic ceramic fuel cell performance at temperatures of 500-700 °C.[2] The high temperatures under which these materials operate have significant effects on material properties and stabilities, and neglecting those effects can lead to considerable inaccuracies. Within each of these systems, we explore the vast compositional space and associated atomic and magnetic disorder and defect formation energies. From our study of SLMA,[3] we identify the range of oxygen vacancy formation energies particularly suited for STC cycles and present a materials design strategy for optimizing oxygen vacancy formation energies through compositional tuning. Our integrated computational and experimental approach provides an assessment of the strengths and limitations of our calculations and offers direction for continued progress in incorporating finite temperature effects into materials by design.

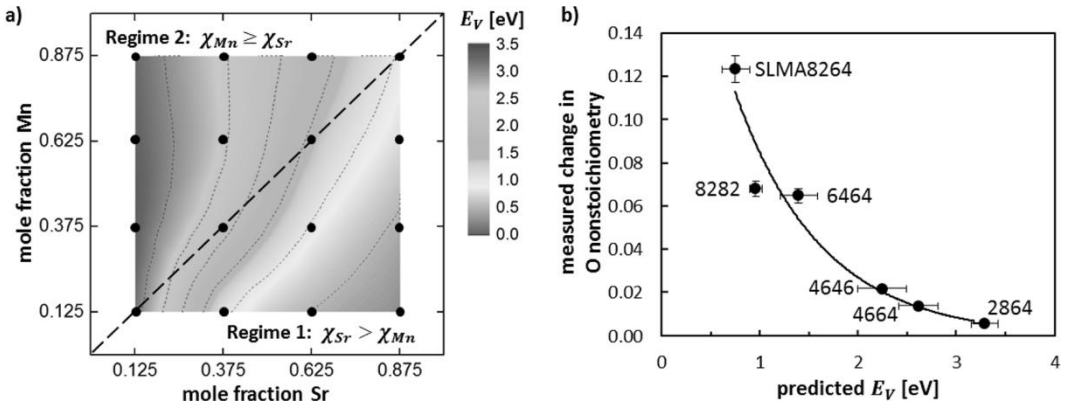

Figure 1 Trends in a) calculated oxygen vacancy formation energies (E_V) as a function of the SLMA composition are supported by good agreement with b) measured changes in oxygen nonstoichiometry under reducing conditions.

References
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