Modeling High Entropy Oxides with DFT and Statistical Mechanics

Grace Chamberlain, Lily Jade Joyce, Dr. Kendra Letchworth-Weaver
James Madison University

High entropy oxides (HEOs) are promising materials for lithium-ion battery cathodes and potential photocatalysts for generation of fuels from sunlight, but experimental discovery and synthesis of new HEOs is expensive and time consuming. These materials have high formation temperatures and become more stable through entropy-driven configurational disorder, so predicting novel HEO compositions with enthalpy-based methods, such as Density Functional Theory (DFT), poses challenges. To overcome these challenges, we created Python-based software which randomizes the placement of atoms in a user-defined lattice type, creating an ensemble of microstates for the local environment of each HEO composition. We use DFT to determine the enthalpy of formation from the single-phase metal oxides for each microstate within the ensemble. Based on the DFT-computed enthalpies of the microstates, we then create a statistical-mechanical model which computes the expectation values and variances of relevant energetic, structural, and electronic properties over the entire ensemble of structures. We explore the sensitivity of our model's predictions to details such as number of microstates and supercell size. For HEOs which experimental groups have synthesized, the efficacy of our approach may be tested by direct comparison to measured formation temperatures as well as bond length distributions determined by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).