Future innovations in renewable energy generation will require the design and discovery of novel materials, where the deliberate incorporation of metastability comes increasingly into focus. Design often starts from a known material, where one aims to modify the properties, for example by changing the composition in alloys. Whereas isostructural alloys are well known and utilized in semiconductor physics (e.g., InGaN), heterostructural alloys between compound with different crystal structures present new opportunities. Using first principles calculations and combinatorial thin-film synthesis, we studied heterostructural alloys such as $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ and $\text{Sn}_{1-x}\text{Ca}_x\text{S}$ [1]. Due to the structural transition around the critical composition, the properties change in a non-linear or even discontinuous fashion, providing a mechanism for materials design that does not exist in conventional isostructural alloys. We show that heterostructural alloys can exhibit a dramatically increased range of metastable alloy compositions between the binodal and spinodal lines, thereby opening up a novel phase space for homogeneous single phase alloys. Metastable heterostructural alloys can also provide access to polymorphic crystal structures that would otherwise require a negative pressure for inducing the phase transition [2], thereby facilitating synthesis of materials with unique properties that would be otherwise difficult to make.

Metastability is also an increasing focus in the discovery of new compounds, including materials that require activated elemental sources for their synthesis. This is often the case for nitrides, which are an important class of materials including examples with exceptional electronic and mechanical properties. When compared to oxides, however, it is striking that there are much fewer known nitride phases, suggesting that nitrides should be an interesting chemical space for exploration and discovery of novel materials, in particular, since nitrides have an exceptional propensity to form metastable structures [3]. As a part of a broader nitrides discovery effort, we have predicted the crystal structures and evaluated the thermodynamic stability ranges (phase diagrams) on the extended scale of non-equilibrium chemical potentials. These efforts identified the previously unknown nitrides $\text{Sn}_2\text{N}_2$, $\text{Ti}_2\text{N}_3$ [4], as well as the ternaries $\text{Zn}_3\text{MoN}_4$, $\text{ZnMoN}_2$ [5], and $\text{Zn}_3\text{SbN}_3$.