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Soft Chemical Approaches to the Synthesis of Metastable Materials

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14. ABSTRACT
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To complement our high-pressure experiments, we developed computational capabilities aimed at mapping high-pressure phase space using unbiased ab initio high-throughput random structure searches. This computational approach not only promoted our understanding of known high-pressure chemistry, it directed our synthetic efforts, resulting in the discovery of the first structurally characterized Mo–Bi intermetallic material. Our computations suggested this material possesses a uniquely stable ordered structure in a region of phase space in which elemental alloying is prevalent. This structure type is also accessed by multiple other Bi transition metal (TM) mixtures at high-pressures, but has not been recovered to ambient conditions. Promisingly, calculations examining the phonon properties of this material reveal a phase change to a lower symmetry polymorph which is stable to ambient pressures and will be pursued experimentally. This result also suggests chemical substitutions across these TM–Bi phases may be a productive route to control their properties and recover them to ambient conditions. A manuscript reporting this discovery and acknowledging AFOSR was recently reported in the Journal of the American Chemical Society.

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Abstract

We synthesized and characterized several new compounds using soft chemistry methods, including: $MoBi_2$, $BiVO_3$, InBi, Cu_3Pb, Ni_3Pb_2, nanoparticles of $Pd_{1-x}Ni_xBi_2$. We also expanded our synthetic studies to ternary compounds with promising transition-metal–Bi sublattices

$MoBi_2$

To complement our high-pressure experiments, we developed computational capabilities aimed at mapping high-pressure phase space using unbiased *ab initio* high-throughput random structure searches. This computational approach not only promoted our understanding of known high-pressure chemistry, it directed our synthetic efforts, resulting in the discovery of the first structurally characterized Mo–Bi intermetallic material. Our computations suggested this material possesses a uniquely stable ordered structure in a region of phase space in which elemental alloying is prevalent. This structure type is also accessed by multiple other Bi transition metal (TM) mixtures at high-pressures, but has not been recovered to ambient conditions. Promisingly, calculations examining the phonon properties of this material reveal a phase change to a lower symmetry polymorph which is stable to ambient pressures and will be pursued experimentally. This result also suggests chemical substitutions across these TM–Bi phases may be a productive route to control their properties and recover them to ambient conditions. A manuscript reporting this discovery and acknowledging AFOSR was recently reported in the *Journal of the American Chemical Society*.[1]

Altman, A. B.; Tamerius, A. D.; Koocher, N. Z.; Meng, Y.; Pickard, C.; Walsh, J. P. S.; Rondinelli, J. M.; Jacobsen, S. D.; Freedman, D. E. *J. Am. Chem. Soc.* **2021**, *143*, 214–222.

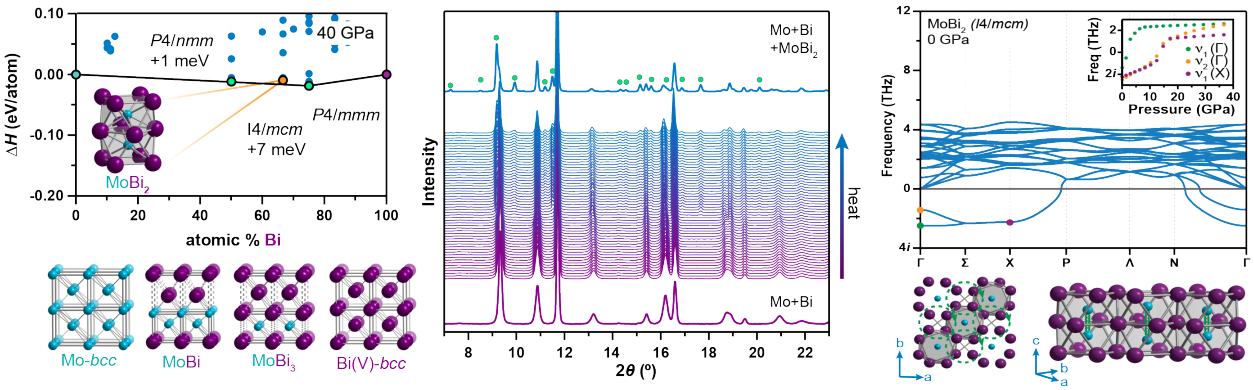

Figure 1: Computationally generated convex hull diagram (left) identified the $MoBi_2$ (center) phase at 40 GPa, which was experimentally realized at 35.8(5) GPa in a laser-heated diamond anvil cell (center). Computational exploration of the phonon properties of this new phase suggest a low symmetry polymorph is dynamically stable to ambient pressures (right).

$BiVO_3$

Following up on our high-pressure discovery of $BiVO_3$, a missing Bi–TM perovskite predicted to be a rare metallic antiferromagnetic oxide,[2] we pursued bulk synthesis techniques to enable further characterization of this novel material. We found evidence that significantly lower pressures are required to access a new polymorph of the material in a multianvil press than in a diamond anvil cell. This difference suggests the form of applied pressure is integral to controlling the pressure dependent redox chemistry required to access this material. We are further exploring the consequences of this observation through planned *in situ* multianvil press experiments and transmission electron microscopy (TEM) experiments utilizing a nano-indenter to apply localized uniaxial pressure. In parallel, we are pursuing *in situ* high-pressure properties measurements to elucidate the pressure dependent magnetic and electronic response of this material. This combined structural and properties study will elucidate the role of pressure in synthesis of this material, promoting synthetic control over the thermodynamic landscape.

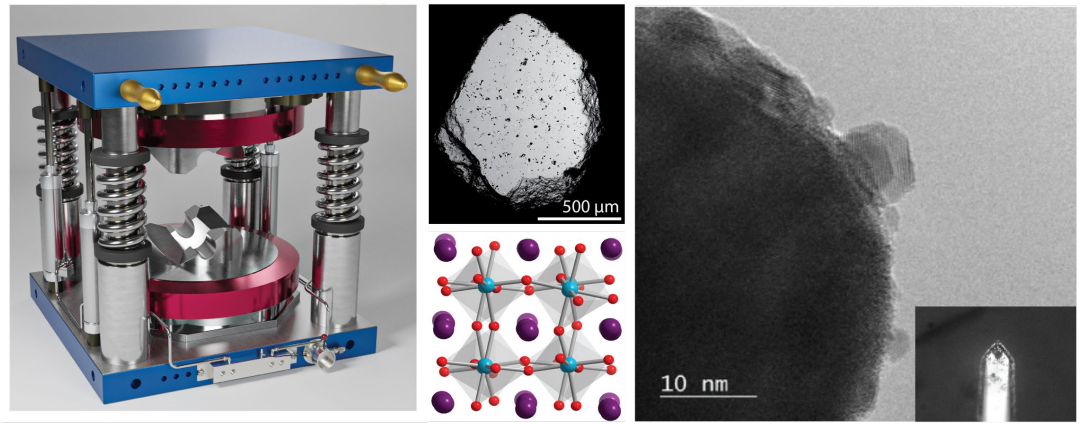

Figure 2: Multi-anvil press (left) experiments performed in 8-3 octahedron assemblies were found to generate samples of $BiVO_3$ (middle top) which possess a low symmetry structure (middle bottom). These samples were further characterized by TEM (right), which will be used to probe localized pressure effects on structure with nano-indenter (right inset).

InBi

Broadening our search for metastable materials and developing a deeper understanding of thermodynamic landscapes in a wider range of chemical systems, we turned our attention to main group metal–bismuth binary systems. Specifically, we investigated the highly unique structure formation behavior in the In–Bi system under high pressure. Our investigation revealed a remarkable deviation from typical solid-state thermodynamic landscapes which normally entail deep thermodynamic minima and high activation barriers. Instead, we observed the anomalous formation of two different site-disordered body centered tetragonal (bct) phases in equilibrium at the same high-pressure high-temperature conditions. The simultaneous formation of these two closely related bct phases suggest that these structures represent nearly degenerate distortions from a body centered cubic structure. Understanding the chemical heuristics that give rise to this unusual thermodynamic landscape and selectively accessing one minimum over another is crucial for manipulating the energy landscape of other material systems and selectively accessing local minima, or metastable materials. Preliminary calculations in this system suggest that neither of the high-pressure bct phases are thermodynamic minima. Instead, we hypothesize that entropy drives the formation of these phases at high temperature. Thus, we are performing phonon calculations and pursuing inelastic neutron scattering measurements to quantify and characterize entropy in this system, elucidating its role in tuning the thermodynamic landscape and giving rise to an observable saddle point.

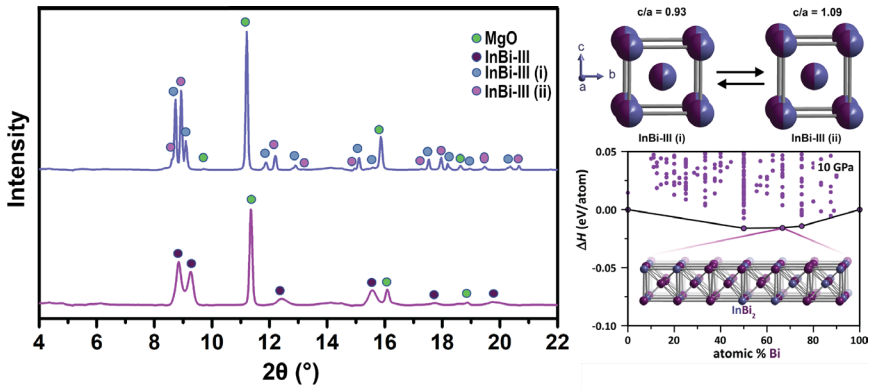

Figure 3: Diffraction pattern of an InBi body centered tetragonal (bct) phase (left) without heating (below) and with heating (above) to anneal out two discrete distortions from the InBi body centered cubic structure. Crystal structures of both bct phases in equilibrium (top right) discovered at high temperature and high pressure identify a potential saddle point in the thermodynamic landscape of the In–Bi system. Convex hull of the In–Bi system (bottom right) aided in mapping disordered bct phases in the thermodynamic landscape and provided insight into the origin of the observed saddle point.

Metastable Nanoparticle Synthesis of $Pd_{1-x}Ni_xBi_2$

We set out to leverage the kinetic control of soft chemical methods and the surface interactions of nanomaterials to create previously inaccessible materials near ambient conditions. Following our discovery of the novel superconductor $NiBi_2$ at high pressure, we aimed to synthesize this material via templated nanoparticle growth on isostructural α-$PdBi_2$. Towards this goal, we developed synthetic routes towards amorphous nanoparticles in the Ni–Bi system. Using these amorphous nanoparticles, we further synthesized nanoparticle heterostructures in the Pd–Ni–Bi system, a chemical system with no reported thermodynamic ternary reactivity. This material has an elemental distribution of $Pd_{0.3}Ni_{0.7}Bi$ with a NiAs structure-type. We currently aim to guide the formation of $NiBi_2$ from amorphous Ni–Bi nanoparticles by tuning their elemental distribution and annealing with an α-$PdBi_2$ template shell. We are also currently working towards elemental mapping of these materials with greater spatial precision to determine the degree to which alloying between all three elements occurs. These new metastable materials synthesized through careful engineering of surface interactions and interfaces provides a model for templating the growth of metastable materials in other systems.

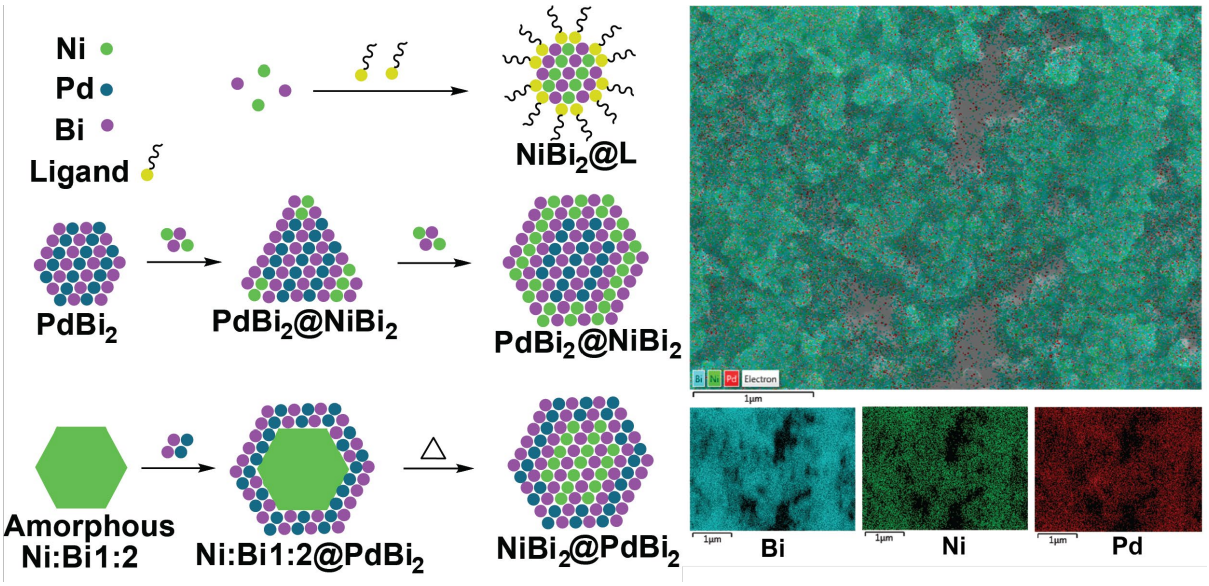

Figure 5. Synthetic approaches towards nanoparticle synthesis of $NiBi_2$, a high-pressure phase in the Ni–Bi system (left). Elemental mapping of Pd–Ni–Bi particles with SEM and EDS (right).

Ni_3Pb_2 PECASE report May 2022

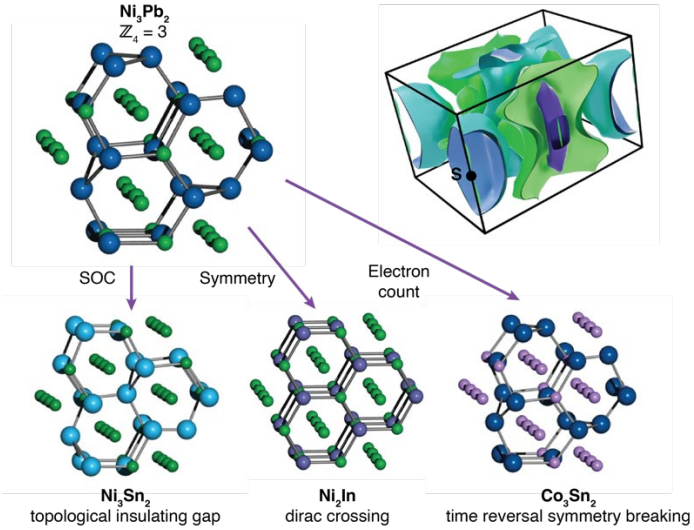

Figure 1. Combination of experimental and computational efforts revealed that Ni_3Pb_2 (top left) exhibits topologically non-trivial behavior (fermi surface shown top right with relevant feature at S point indicated). This material completes a structurally related but chemically flexible family of transition metal- heavy main group materials (bottom) where chemical composition determines overall symmetry and thus topological character. These define chemical axes that may be tuned synthetically through doping experiments to control topological behavior.

Employing a large volume press, we synthesized Ni_3Pb_2, the first bulk binary phase in the Ni–Pb system. Our unique high-pressure flux approach allowed for the isolation of high-quality single crystals, whose structure could be resolved with single crystal X-ray diffraction. The precise atomic positions elucidated by this experiment revealed a chemically flexible system where chemical composition subtly but significantly tweaks the overall symmetry of the material. Because symmetry is deterministic of electronic structure topology in solid-state materials, computational efforts demonstrated that Ni_3Pb_2 completes a family of structurally related transition metal-heavy main group intermetallic materials with non-trivial topology. Together, they define the endpoints of a promising chemical platform of synthetically tunable topological materials. Tamerius, A. D.*; Altman, A. B.*; Waters, M. J.; Riesel, E. A.; Malliakas, C. D.; Whitaker, M. L.; Yu, T.; Fabbris, G.; Meng, Y.; Haskel, D.; Wang, Y.; Jacobsen, S. D.; Rondinelli, J. M.; Freedman, D. E. *J. Am. Chem. Soc.* **2022**, *144*, 11943-11948.

Ongoing Projects

We plan to continue to widen our synthetic approach toward metastable materials via electrochemical post-synthetic manipulation of known ternary compounds with promising TM–Bi sublattices. To this end, we have adopted a two-fold approach: 1) reduction of ternary TM–Bi–I materials, which have been previously reduced to the known intermetallic as exemplified by Ni-Bi-I system which reduced to $NiBi_3$, and 2) oxidation of Ti–TM–Bi materials, where the TM–Bi sublattices are isostructural to metastable materials our group has discovered at high pressure. In particular, the Ti–TM–Bi system is an ideal starting point for this approach as it includes Ti_4CrBi_2, Ti_4MnBi_2, and Ti_4FeBi_2 which host the same TM–Bi sublattice as the high pressure $MoBi_2$, $MnBi_2$, and $FeBi_2$ phases. By examining the gradual decrease in concentration of Ti and I, we can explore how Ti and I affects stability of the structure and its properties. This will provide further insight into how to best recover these metastable phases at ambient conditions. More generally,

understanding gained from these post-synthetic deintercalation attempts can be applied to other systems to access new materials.

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