

**Nitrides** are an exciting class of solid-state compounds, with unique structures and compelling properties for next-generation functional materials.

Unfortunately, nitrides are rare in nature and difficult to synthesize. **There are only ~300 unique ternary metal nitrides in the ICSD, in contrast to over 4,000 ternary metal oxides.**

We employ a suite of **high-throughput computational materials discovery tools** to broadly survey stability relationships across the inorganic ternary metal nitrides.

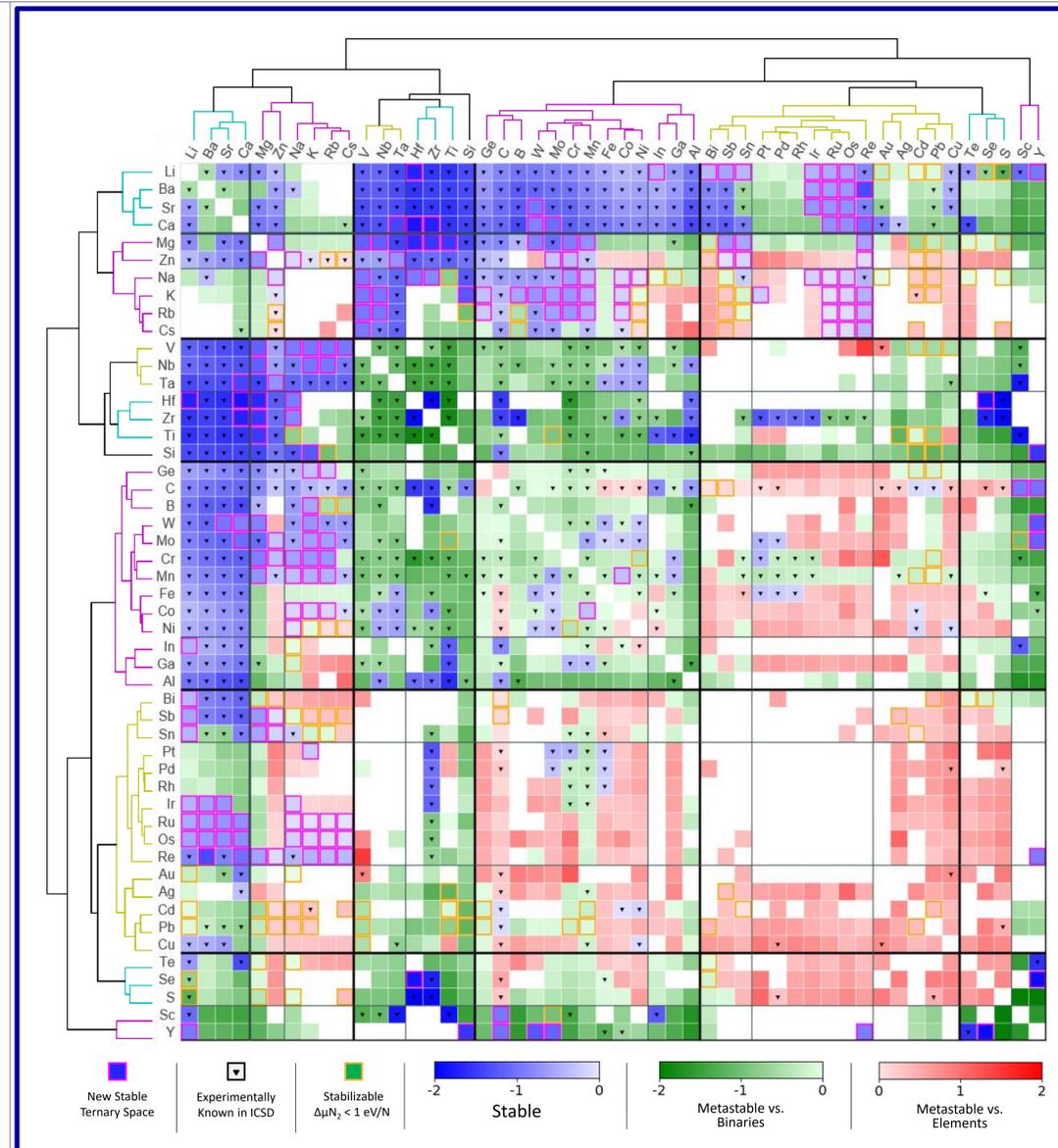
By **clustering** the ternary nitrides into chemical families with distinct stability and metastability, we produce a map that visualizes both promising and risky compositions for further exploratory synthesis.

We reveal the fascinating interplay between chemistry, nitride composition, and solid-state bonding in governing the stability of ternary nitrides.

Ternary M <sub>1</sub> -M <sub>2</sub> -N Spaces	Previously Known	Newly Predicted	Portion of map
Stable Ternary Systems (Blue)	189	92	281 (26%)
- Stable Alkali-Metal-Nitride Systems	124	76	200
- Stable Metal-Metal-Nitride Systems	65	16	81
Metastable vs. Stable Binaries, ΔH <sub>f</sub> < 0 (Green)	98	322	420 (44%)
Metastable vs. Elements, ΔH <sub>f</sub> > 0 (Red)	20	241	261 (27%)

Ternary A <sub>x</sub> B <sub>y</sub> N <sub>z</sub> Phases	Previously Known	Newly Predicted	Total Number
Stable Ternary Phases	213	203	416
Metastable, ΔE <sub>Hull</sub> < 70 meV/atom	39	36	75
Metastable, ΔE <sub>Hull</sub> < 200 meV/atom	85	175	260
Metastable: Stabilizable Δμ <sub>N</sub> < +1 eV/N	3	92	95

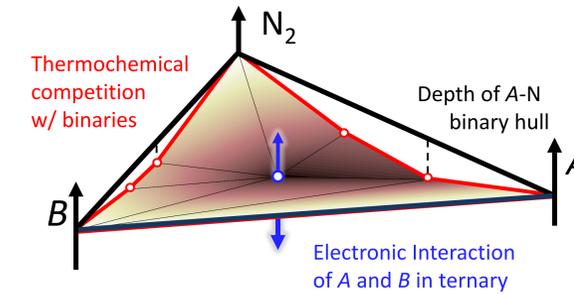


## How does chemistry drive the stability of the ternary metal nitrides?

Stable ternary nitrides lie on the convex hull, shown on the right. The energy of a ternary nitride can be expressed relative to the hull as

$$\Delta E_{\text{Hull}} = E_{A-B-N} - E_{A-N} - E_{B-N}$$

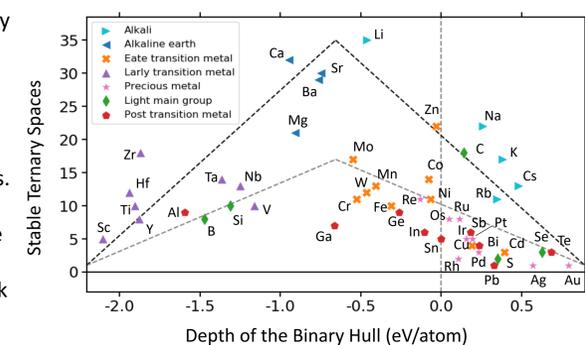
We explain ternary stability from 1.) stability of the competing binaries, and 2.) quantum chemical solid-state bonding in the ternary.



### Thermochemical competition with binary nitrides

'Depth of the Binary Hull' is the energy of lowest-energy binary nitride in a Me-N space, and serves as a proxy for the strength of the solid-state metal-nitrogen bond

When plotting stable ternary spaces vs. depth of binary hull, a 'volcano' plot emerges, where ternaries are unstable against binaries with deep hulls, or do not form at all if Me-N bonding is weak in the first place.

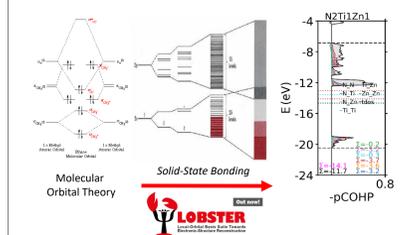


Alkali and Alkaline Earth form stable ternaries more readily than elements with similar hull depth.

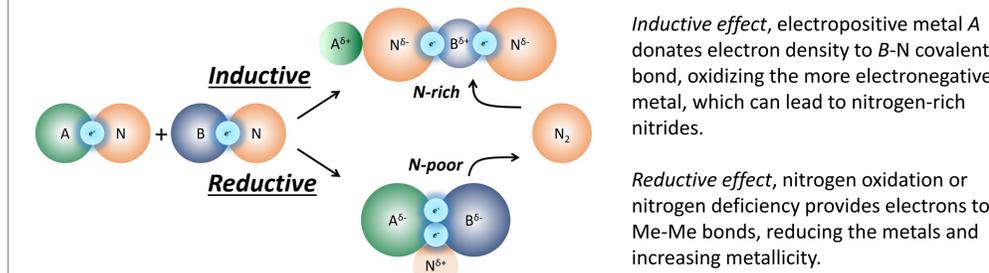
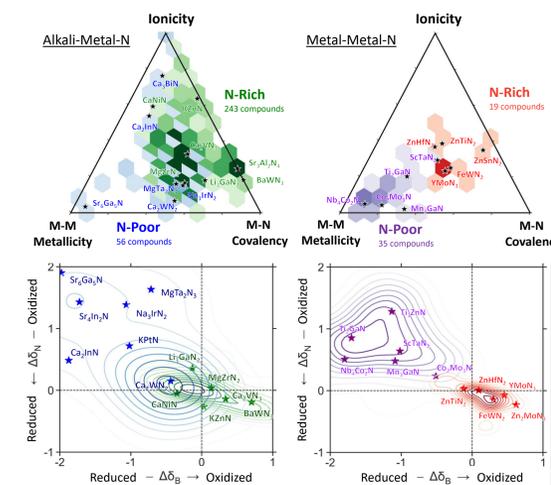
M-N bonds are very strong (Blue), Intermediate (Green), M-N bonds are weak (Red). Binaries are too stable, Ternaries likely to decompose (Red), Good to form ternaries nitrides with (Green), Nitrides unlikely to form in this chemistry (Red).

### Electronic Interaction of A and B in ternary

We conduct a large-scale data-mining analysis of chemistry, nitride composition, and solid-state bonding in governing the stability of 353 ternary metal nitrides.

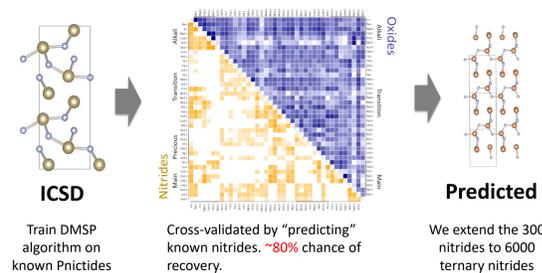


**Metallicity:** COHP-computed A-A, B-B, A-B and bonds  
**Covalency:** COHP-computed A-N, B-N, and N-N bonds  
**Ionicity:** Ratio of Net Atomic Charges (NAC) over the Summed Bond Order (SBO) obtained from the Density Derived Electrostatic and Chemical (DDEC)



## CONSTRUCTION OF THE MAP

Data-mined ionic substitution suggests new ternary nitride structures based on rational ionic substitutions on known phases

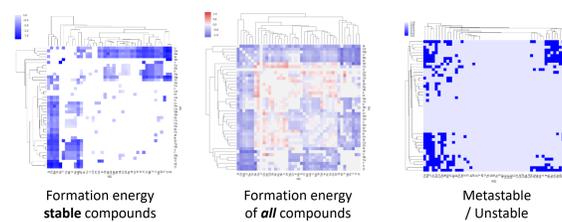


We evaluate phase stability of DMSF-predicted structures using tools within the Pymatgen and Materials Project infrastructure

DMSF offers an efficient way to probe both nitride structures and stoichiometries over a broad compositional space.

DMSF may not predict the ground-state structure if a prototype structure does not exist. However, identification of a ternary with ΔH<sub>f</sub> < 0 in an otherwise empty space highlights that space for further investigations of ground-state structures.

Multi-Feature Hierarchical Agglomeration reveals underlying relationships and chemical families across the ternary metal nitrides chemical space



Clustering on individual features gives cluster maps with limited scope.

We develop a multi-feature distance metric that captures high-level stability trends and local-scale chemical relationships

**Multi-factor Clustering:**  
 - Formation Energies  
 - Stable/Metastable/Unstable  
 - Chemical group

**Data-Type**  
 Continuous  
 Nominal  
 Ordinal

**Gower Metric:**

$$G_{M_1-M_2} = \sum_i W_i \cdot d_{M_1-M_2}^i$$

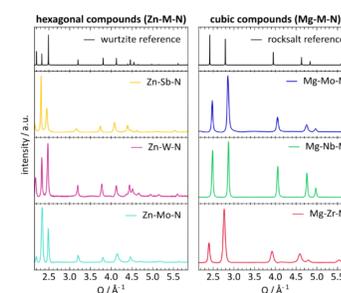
Linear combination of distance metrics with user-assigned weights

## SYNTHESIS OF NEW NITRIDES

We use reactive sputtering to synthesize 10+ new Zn- and Mg- based ternary nitrides

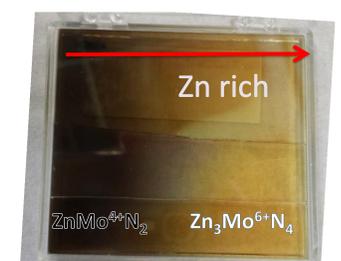
Mg-based ternary nitrides tend to crystallize in rocksalt-derived structures, whereas Zn-based ternary nitrides form in a Wurtzite-derived structure

New ternary nitrides are all semiconductors with E<sub>gap</sub> ~ 1-2 eV



By changing the Zn:Mo ratio in Zn-Mo-N ternaries, we can modulate the molybdenum oxidation state from Mo<sup>4+</sup> to Mo<sup>6+</sup>, turning metallic ZnMoN<sub>2</sub> into a wide-bandgap Zn<sub>3</sub>MoN<sub>4</sub> semiconductor

This redox-mediated behavior suggests a new class of II<sub>x</sub>-TM-N semiconductors, with tunable optoelectronic properties.



"Redox Mediated Stability in Zinc Molybdenum Nitrides Elisabetta Arca et al., JACS, (2018)"