Collaborative research charts course to hundreds of new nitrides

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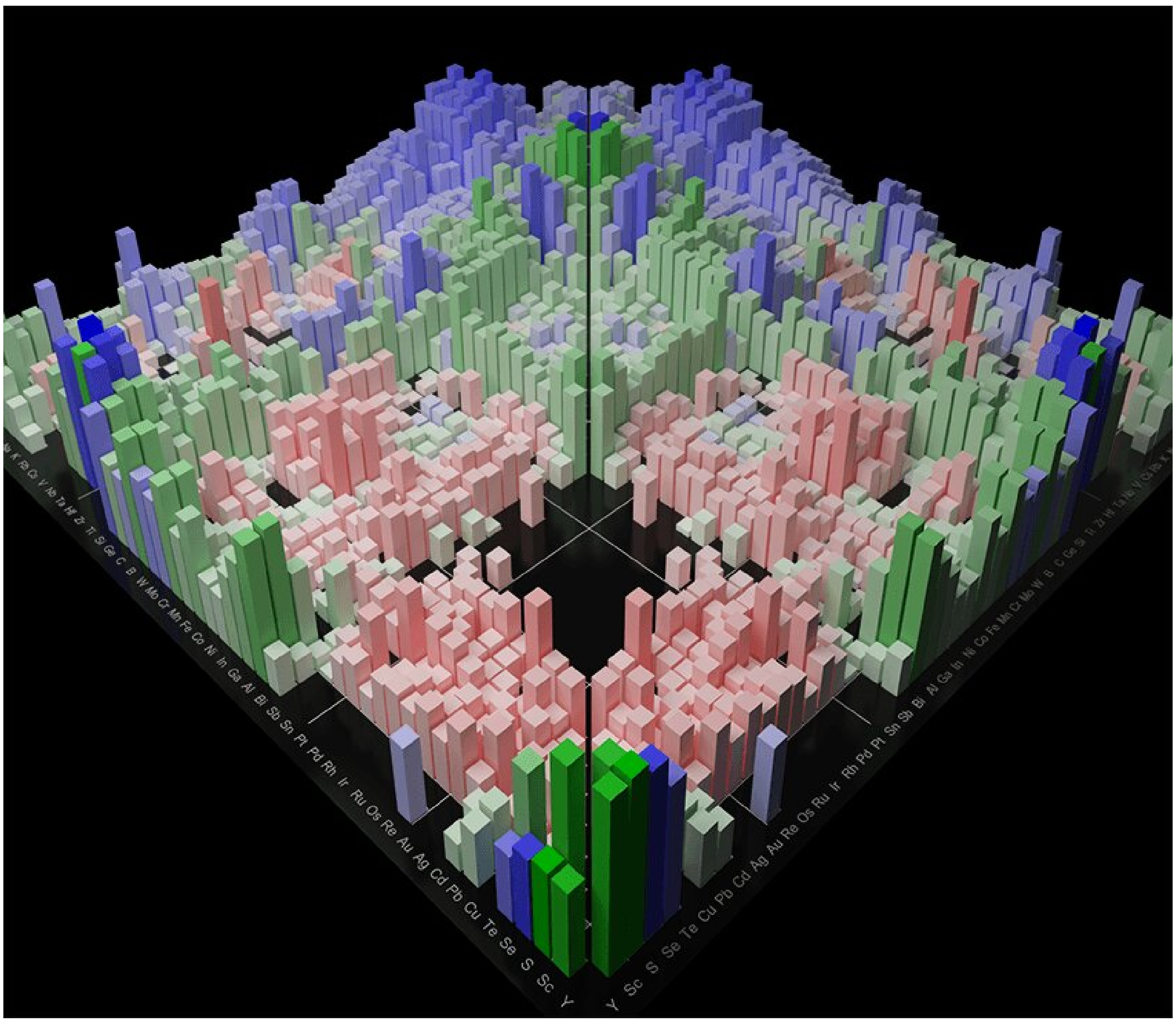

The researchers were able to map out where new nitrides could be found. Credit: Josh Bauer/NREL

Andriy Zakutayev knows the odds of a scientist stumbling across a new nitride mineral are about the same as a ship happening upon a previously undiscovered landmass.

"If you find any nitride in nature, it's probably in a meteorite," said Zakutayev, a scientist at the U.S. Department of Energy's (DOE's) National Renewable Energy Laboratory (NREL).

Formed when metallic elements combine with nitrogen, nitrides can possess unique properties with potential applications spanning from semiconductors to industrial coatings. One nitride semiconductor served as the cornerstone of a Nobel Prize-winning technology for light-emitting diodes (LEDs). But before nitrides can be put to use, they first must be discovered—and now, researchers have a map to guide them.

A groundbreaking research effort involving scientists at NREL; Lawrence Berkeley National Laboratory (LBNL); University of Colorado, Boulder (CU); and other partner institutions around the country recently published "A Map of the Inorganic Ternary Metal Nitrides," which appears in *Nature Materials*. The paper features a large stability map of the ternary nitrides, highlighting nitride compositions where experimental discovery is promising, and other compositions where nitride formation would be unlikely. For chemists attempting to create new nitrides in the laboratory, this map will be a significantly valuable tool.

Wenhao Sun, lead author of the paper and staff scientist at LBNL, likened materials discovery to the world exploration of bygone days. "Sailing into the unknown was a very risky endeavor," Sun explains, "and in the same way, exploration of new chemical spaces can also be risky. If you go into the lab and mix different elements together, you might make a new compound. Or you might not. If you don't find a new material where you are looking, it can be a big waste of time and effort. Maps help to guide explorers, allowing them to navigate better. Here, we built a chemical map to guide the exploratory synthesis of nitrides."

An interactive version of the map shows stable ternary nitrides highlighted in blue, indicating that they are good candidates for experimentation.

Other research funded by the center has discovered new ways to combine materials to form alloys, as well as to synthesize specific material polymorphs that could form the basis of next-generation semiconductors. The new nitrides research follows several years of investigating metastable materials and the potential to use them in various technologies, including semiconductors.

Exploring Metastable Materials

Metastable materials are those that, over time, will shift to become more stable. Diamonds, for example, are metastable as they would eventually turn into graphite, a more stable polymorph form of carbon. But the amount of time that takes is considerable—millions of years in this example—so researchers should not discount the use of metastable compounds.

"If you only do materials design with stable materials," Sun said, "your choices are limited. But if you start thinking about which metastable materials can be made, you increase your design space."

"Our EFRC team set out to include metastable compounds into materials design," added Tumas. "This work demonstrates the power of collaborations between theorists and experimentalists, combining computational, synthetic, and characterization skills in a team approach."

In addition to NREL, CU, and LBNL, scientists from Oregon State

University and SLAC National Accelerator Laboratory lent their expertise in mapping, characterizing, and understanding the potential new nitrides. "This was very much a team effort," said Sun. "It definitely took everyone working together."

Before embarking on his ongoing collaboration with NREL, Sun had determined that metastable materials accounted for a significant fraction of nitride compounds, and published his findings near the end of 2016. "After that was written, it became clear this would be a good team effort to explore nitrides," Sun said. "NREL has been making metastable nitrides for many years now."

That, coupled with NREL's demonstrated ability to synthesize highly metastable nitride thin-films (described in Zakutayev's 2016 review article on this topic), inspired an article on binary nitrides that Sun, Zakutayev, and others published in 2017. The newly published research on ternary nitrides was the next logical step.

The world of ternary nitrides hasn't been thoroughly explored because the compounds—consisting of nitrogen and two metals—are difficult to synthesize. The prediction of the new ternary nitrides relied on computational materials science, using machine-learning algorithms to map previously uncharted spaces. This accelerated the process compared to the traditional trial-and-error method.

More Nitrides on the Horizon

Although nitrogen is far more abundant in Earth's atmosphere than oxygen, it's considerably easier for oxides to form than nitrides. Leave a piece of iron outside, for example, and eventually it will rust, or oxidize. That's because the bond between oxygen atoms can easily dislodge. But nitrogen atoms hold tight.

"Oxides and nitrides often have a similar chemistry," said Zakutayev, who works on developing new materials for renewable energy technologies and has a proven track record in synthesizing nitrides. "But for each nitride documented, there are 14 oxides. If the chemistry is similar, there is no reason there should be many of one and few of the other. That's a very large discovery opportunity."

Before researchers could map the nitrides, however, they first needed to predict new nitride materials. Using high-throughput computational materials science, they first considered 6,000 potential nitride compounds by substituting known nitrides with new elements. After checking the stability of these possible nitrides, they predicted 203 new stable ternary nitride compounds. Until now, only 213 stable nitrides were known to exist.

The first two ternary nitrides were discovered in 1927, and the third eight years later. Since then, new nitrides have been discovered sporadically. This batch of 203 is by far the largest number of potential new nitrides identified in a single year.

"Historically, nitrides are discovered at the rate of three or four a year, experimentally speaking," said Zakutayev.

Guided by the map, Zakutayev and his team were initially able to synthesize seven new ternary nitrides in the laboratory. Several more nitrides have been synthesized since the paper was written.

Synthesis Proves Accuracy of Predictions

"So far, we're batting a thousand," said Holder, a research professor who holds a joint CU-NREL appointment and is a co-author of the new paper. "Every ternary nitride we predicted could make a stable compound."

The ability to synthesize the seven new nitrides, the authors noted in the paper, validates the predictions of the existence of the other nitrides "and highlights the valuable role of computational materials discovery in accelerating exploratory synthesis in novel chemical spaces."

The research also provides another dimension to the periodic table of elements by indicating a group of metals' propensity to form stable or metastable ternary nitrides. Calcium, for example, stood out for its ability to create a nitride. So did lithium. The scientists also were able to discount metals that won't be useful in nitride research. "Gold doesn't want to combine with nitrogen," Holder said, "and adding another metal is not going to stabilize it enough to make it happen."

Now possessed with a greater understanding of nitrides, researchers can move forward with determining their best uses. The Nobel Prize for physics in 2014 was awarded to a trio of researchers who combined several layers of gallium nitride to invent a blue LED. Coupling their blue light with efficient phosphors allowed the creation of long-lasting and energy-efficient white LED bulbs. The nitrides team sees even more applications on—and beyond—the horizon.

"Certainly, these materials have many possible new functional applications," Sun said. "Some of them are semiconductors and others might be superconductors. Many of them might have applications we haven't even dreamed of yet. There are a lot of directions for this to go."

More information: Wenhao Sun et al. The thermodynamic scale of inorganic crystalline metastability, *Science Advances* (2016). DOI: 10.1126/sciadv.1600225

Wenhao Sun et al. A map of the inorganic ternary metal nitrides, *Nature Materials* (2019). DOI: 10.1038/s41563-019-0396-2

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