The Mystery of the Missing Materials

Stay alert, Sherlock Holmes. The Center for Inverse Design is "afoot"!

The Center (CID)—an Office of Science Energy Frontier Research Center—is in hot pursuit of new materials with extraordinary properties. And under CID's magnifying glass is the vast materials space containing the promising A_2BX_4 spinel metal-chalcogenide and ABX half-Heusler tetrahedral compounds, which have great potential for solar-cell and other electronic and optical applications.

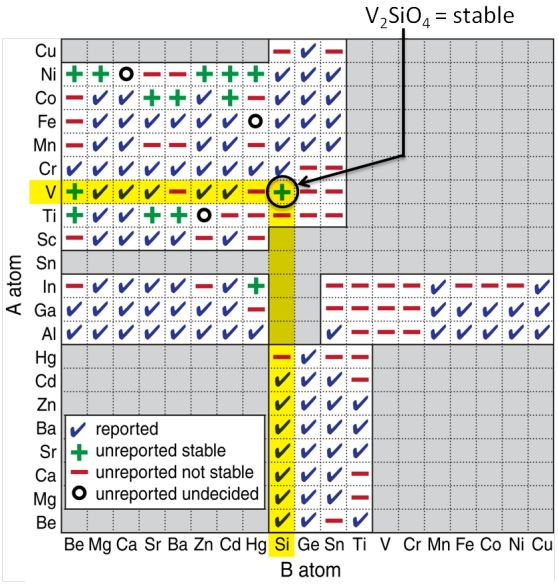
Curiously and unexpectedly, when CID researchers turned to the highly respected compilations of documented inorganic compounds, they found that most families of these interesting materials were *missing*!

- Were they not feasible thermodynamically?
- Or were they simply impossible to synthesize?
- Or were they somehow overlooked by those meticulous encyclopedias amassed by Inorganic Crystal Structure Database, Bergerhoff and Brown, the International Centre for Diffraction Data Power Diffraction Files, and Wyckoff?

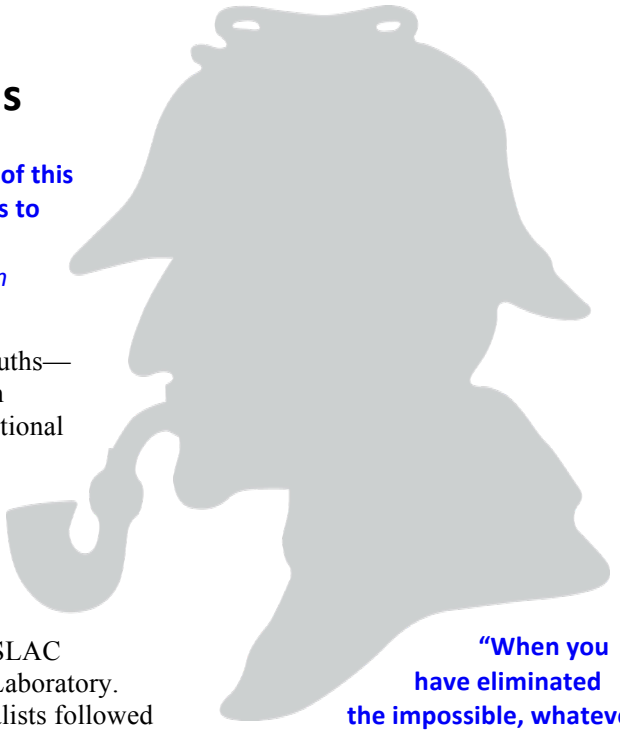
For example, in examining the A_2BX_4 spinel compounds, there are 684 possible combinations of elements that may be tabulated. Yet, only 255 combinations have been reported. For the 714 ABX compounds, only 226 are in the literature. The mystery is: *What happened to the missing 429 spinels and the 488 half-Heuslers?*

"In solving a problem of this sort, the grand thing is to be able to reason backward." (*A Study in Scarlet*, 1887)

Enter the scientific sleuths—the CID inverse design partners—from the National Renewable Energy Laboratory (NREL), University of Colorado– Boulder, Northwestern University, Oregon State University, and SLAC National Accelerator Laboratory. First, the theory specialists followed the CID-developed inverse design methodology: consider design principles that relate to materials being possible because of their thermodynamic stability. *Can inverse design find some evidence for the existence of these missing materials?*



Matrix for A_2BO_4 showing that of the 164 possibilities, only 101 compounds are reported. Of the 63 unreported compounds, 14 are stable, 49 are not stable, and 3 are still undetermined. V_2SiO_4 is highlighted as unreported, but predicted to be stable.



"When you have eliminated the impossible, whatever remains, however improbable, must be the truth." (*Sign of the Four*, 1890)

The high-throughput screening of these materials is illustrated for the case of V_2SiO_4, an oxide spinel. Applying first-principles thermodynamic theory, the scientists calculated the energy of formation for each possible combination of elements in the spinel (see the matrix below).

Results of chemical potential calculations were also plotted onto triangle diagrams for pairs of elements (e.g., see the V-Si oxide triangles on the bottom of the next page). By eliminating all the other non-spinel phases, researchers discovered a "sliver" of possibilities—an undiscovered material that should be stable according to it predicted pressure and temperature conditions. A missing material was discovered.

"There was not one of them which I did not apply to the inquiry. And it ended by my discovering traces, but very different ones from those which I had expected." *(The Adventure of the Crooked Man*, 1893)

This procedure was applied to the entire A_2BX_4 spinel family. And the result? Of the 429 unreported A_2BX_4 metal-chalcogenides, about 100 were determined to be able to exist as stable compounds—including 14 oxides, 34 sulfides, 28 selenides, and 24 tellurides. The mystery of the missing materials was on its way to being solved. And the CID has now engaged an integrated experimental process to synthesize these potentially valuable candidates for electronic applications.

"The theories which I have expressed, and which appear to you to be so chimerical, are really extremely practical..." (*A Study in Scarlet*, 1887), and
"Never theorize before you have data. Invariably, you end up twisting facts to suit theories, instead of theories to suit facts." (*A Scandal in Bohemia*, 1892)

To be successful in solving the mystery, experimentalists work hand-in-hand with the theorists within the inverse design process. For the case of spinels, scientists have just begun experimental validation and have already found several of the missing compounds to exist, such as V_2SiO_4, $Co_2(Br,Sr)O_4$, and Ti_2ZnO_4. For the half-Heuslers, several have been shown to exist experimentally, validating the theoretical prediction and the Inverse Design methodology. Work will continue on making the other predicted compounds. But for some compounds, the task will be nearly impossible because they only exist in such a narrow range of temperature and pressure conditions.

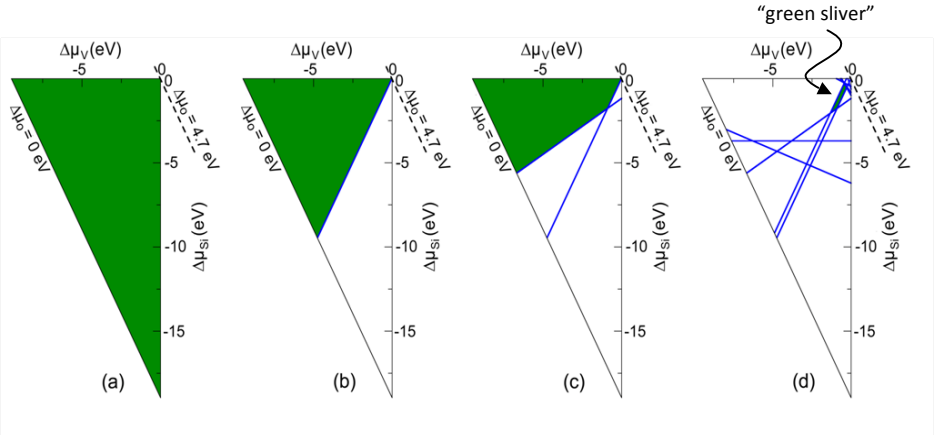
Inverse design is working in a practical sense. But this is not the final solution—rather, it is only the first step in demonstrating practicality. Meanwhile, scientists are already applying their theory tools to a new set of design principles, with the goal of uncovering other materials that exhibit the desired extraordinary electronic and optical properties.

This work is taking inverse design to its intended next level of discovery—*functionality*. Are these spinels superior transparent conducting oxides? Can an ABX half-Heusler composed of three metals really be a PV semiconductor?

"You know my methods. Apply them." (*Sign of the Four*, 1890)

The primary focus of the Center for Inverse Design is the science of inverse design and materials discovery. But a major goal of the Center also includes outreach: "To promote the Inverse Design methodology and tools within the scientific community as a user-friendly, transferable approach for solving problems in materials science." The success of the Center is tied to bringing this revolutionary way of doing materials science to the scientific community.

It's "elementary"!



Series of "stability triangles" for the V-Si-O systems, showing results of inverse design calculations through elimination of competing phases (a) V, Si elements, (b) VO, (c) VO_2, (d) SiO_2, V_2O_3, V_2O_5, V_6Si_5, V_3Si, VSi_2, V_5Si_3, leaving a "green sliver" for a stable V_2SiO_4 compound that was missing from compilations of reported materials.

For more information:

- X. Zhang, V. Stevanovi, M. d'Avezac, S. Lany, and Alex Zunger, "Discovery of unreported A_2BX_4 metal-chalcogenide compounds via first-principles thermodynamics," *Phys. Rev. B* (submitted), 2011.
- X.W. Zhang and A. Zunger, "Diagrammatic separation of different crystal structures of A_2BX_4 compounds without energy minimization: a pseudopotential orbital radii approach," *Advanced Functional Materials* **20**, 1944–1952 (2010). DOI: 10.1002/adfm.200901811.
- X. Zhang, L. Yu, A. Zakutayev, and A. Zunger, "Sorting out stable vs. unstable hypothetical compounds: The case of multifunctional ABX Half-Heusler filled tetrahedral structures," *Advanced Functional Materials*, accepted for publication, 2011.
- Sir Arthur Conan Doyle, **The Complete Sherlock Holmes**, Doubleday, New York, 1930.

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