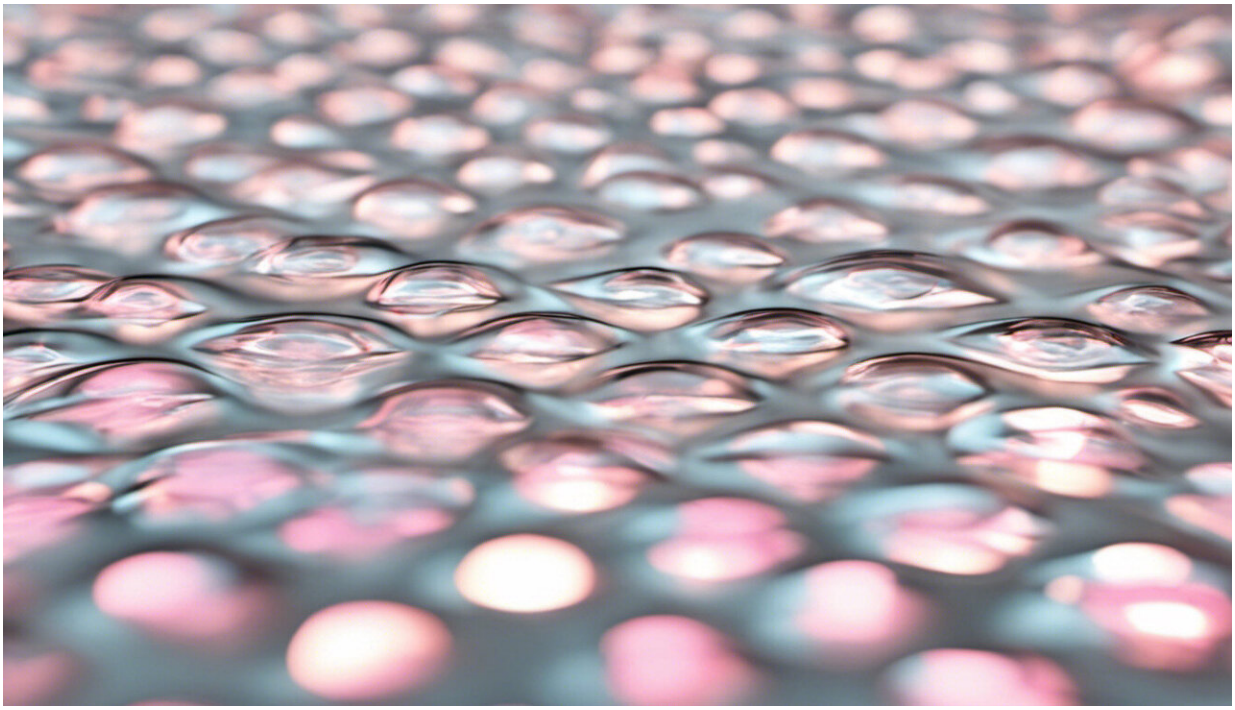
Counting perovskites

May 10 2018



Credit: AI-generated image (disclaimer)

Marina Filip, Postdoctoral Research Assistant, and Feliciano Giustino, Professor of Materials, both in the Department of Materials, explain how elementary geometry and modern data analytics can be combined to predict the existence of thousands of new materials called 'perovskites', as shown in their recent publication in *PNAS*.

Perovskites are a broad family of crystals that share the same structural

arrangement as the mineral $CaTiO_3$. The extraordinary appeal of perovskites is their unusual chemical versatility, as they generally can incorporate almost every element in the Periodic Table. This leads to an incredibly diverse array of functionalities. For example, two major scientific discoveries of our times prominently feature perovskites, high-temperature superconductivity in perovskite cuprates (Bednorz and Müller, Nobel Prize 1987) and the recent discovery of the perovskite solar cells (Snaith, University of Oxford 2012).

In our own study we wanted to understand what makes certain combinations of elements in the Periodic Table arrange as perovskite crystals and others not, and whether we could anticipate how many and which perovskites are yet to be discovered.

It turned out that Norwegian mineralogist Victor Goldschmidt asked exactly the same question in 1926. Based on empirical observations, he proposed that the formability of perovskites follows a simple geometric principle, namely: The number of anions surrounding a cation tends to be as large as possible, subject to the condition that all anions touch the cation. This statement is known as the 'no-rattling' hypothesis, and essentially means that if we describe a crystal using a model of rigid spheres, in a perovskite the spheres tend to be tightly packed, so that none can move around freely. Using elementary geometry Goldschmidt's hypothesis can be translated into a set of six simple mathematical rules that must be obeyed by the ions of a perovskite.

Goldschmidt's hypothesis had been used in one form or another in countless studies over the last century, in order to explain the formation of perovskites in qualitative terms, but its predictive power had never been assessed quantitatively. We realized that unlike 1926, in 2018 we benefit from a century of research in crystallography, documented in publicly available databases of crystal structures, such as the Inorganic Crystal Structure Database, and more than 50,000 published scientific

papers on perovskite compounds. Using internet data-mining and statistical analysis, we were able to collect and study a library of more than 2000 chemical compounds which are known to form in various crystal structures, and use them to test the predictive power of Goldschmidt's hypothesis. We found that this very elegant geometric model is actually capable of discriminating between compounds which are perovskites and those which are not with a higher success rate than sophisticated quantum-mechanical approaches.

In our study we used this simple model to screen through nearly four million compositions, and predict the existence of more than 90,000 new perovskite materials that have not been synthesized yet. This library of predicted compounds offers the exciting challenge of uncovering the functionalities of these novel perovskites to the community working on the synthesis and characterization of new materials. Most importantly, our discovery may lead to the realization of entirely new functional materials for a broad range of technologies, from applications in energy, electronics and medicine.

More information: The geometric blueprint of perovskites. *PNAS*. doi.org/10.1073/pnas.1719179115

Provided by University of Oxford