

Unusual defect physics underlies perovskite solar cells' exceptional performance

First-principles calculations provide insight into one of the newest and most promising classes of materials for photovoltaic devices.

Despite decades of research into new technologies and materials for solar energy conversion, the vast majority of the photovoltaic cells in use are based on crystalline silicon wafers. With few exceptions, other proposed solar-cell designs incorporate rare and costly chemical elements, require expensive fabrication techniques, or convert little of the incident light to electricity. The perfect balance between low cost and high performance has remained elusive.

Solar cells based on a class of materials called organometal halide perovskites have recently and rapidly emerged as one of the most promising contenders yet. Last year, just four years after the cells' debut, two groups independently reported perovskite solar cells with power-conversion efficiencies of 15%. (Commercial silicon-wafer cells are about 20% efficient.) There's no obvious reason to suspect that that's anywhere near their efficiency limit. But

much remains unknown about why the perovskites work so well.

Now Yanfa Yan, Wanjian Yin, and Tingting Shi, of the University of Toledo in Ohio, have used density functional theory to study the perovskites' defect physics.¹ They've uncovered some unusual properties that may help shed new light on the cells' performance and how they can be improved.

High efficiency

A perovskite is any material with the formula ABX_3 , where A and B are cations and X is an anion, and with the cubic crystal structure shown in figure 1a. (The original perovskite, the mineral $CaTiO_3$, was discovered in the Ural Mountains and named for Russian mineralogist Lev Perovski.) In the solar-cell perovskites, A is a polyatomic organic cation, usually methylammonium ($CH_3NH_3^+$); B is a large atomic ion, usually lead; and X is a halogen—either chlorine, bromine,

iodine, or some combination of the three.

All of those constituent elements are abundant. And the perovskites can be produced by solution processing, one of the cheapest methods available. Films of the iodide perovskite $CH_3NH_3PbI_3$, for example, can be made from CH_3NH_3I and PbI_2 dissolved in a common solvent.

The perovskites were originally used as a replacement for the dye in a dye-sensitized solar cell,² a general solar-cell architecture first described in 1991 by Brian O'Regan and Michael Grätzel.³ As shown in figure 1b, a thin layer of perovskite coats a mesoporous film of titanium dioxide. Absorbed sunlight excites the perovskite's electrons, which are then injected into the TiO_2 conduction band and conveyed to the cell's anode (made from the optically transparent but electrically conducting fluorine-doped tin oxide). The holes left behind are transported to the cathode.

In the first perovskite solar cells, as in the original dye-sensitized cells, the hole-transporting material was a liquid electrolyte solution; more recent devices employ an organic semiconductor.

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In July 2013 Grätzel and his group at the Swiss Federal Institute of Technology in Lausanne reported a 15% power-conversion efficiency from an iodide perovskite dye-sensitized cell.⁴

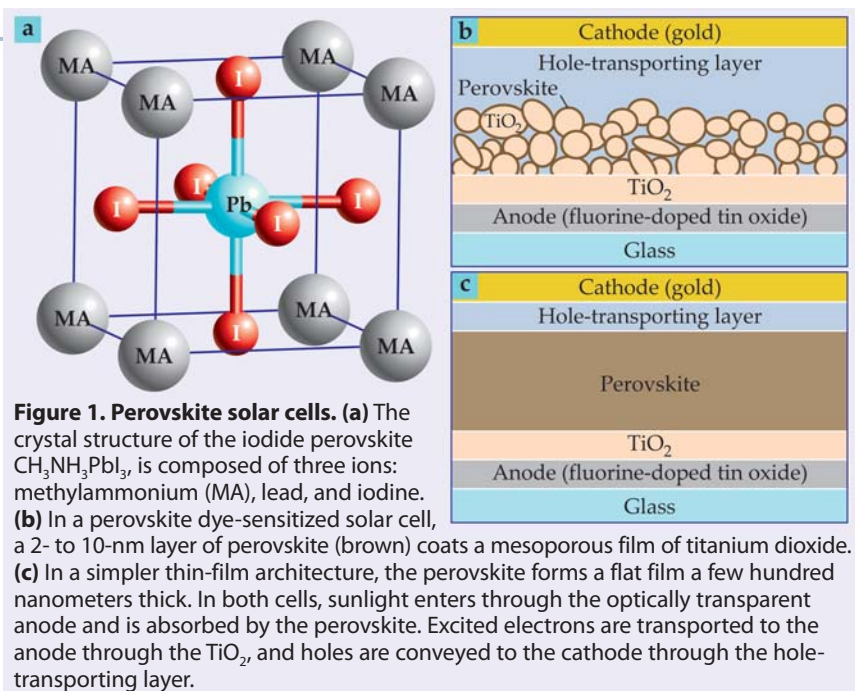
In that design, the perovskite's only function is to absorb light and produce charge carriers. The perovskite layer is so thin—between 2 nm and 10 nm—that its charge-transport properties don't come into play. But in 2012 Henry Snaith and colleagues at Oxford University reported on a cell they'd made in which the mesoporous TiO_2 was replaced with mesoporous alumina, an electrical insulator.⁵ The Al_2O_3 just served as a scaffold to support the perovskite layer (Snaith and company used the mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{1-x}\text{Cl}_x$), and electrons had to travel to the anode through the perovskite itself. Not only did the device still work, but its efficiency was slightly improved over the equivalent TiO_2 cell.

That success raised the possibility of eliminating the mesoporous layer entirely and using the simpler, potentially cheaper thin-film architecture shown in figure 1c. And Snaith and colleagues did just that: In September 2013 they reported a 15%-efficiency cell with a 330-nm-thick film of mixed-halide perovskite.⁶ They'd made the film by vapor deposition rather than the cheaper solution processing because of the difficulty in creating a uniform flat film by solution-based methods.⁷

It's unusual for a solution-processable material to be able to transport charge carriers more than 10 nm, let alone 330. Grätzel (in collaboration with Tze Chien Sum of Nanyang Technological University in Singapore) and Snaith both investigated the perovskite charge-transport properties more directly; they found transport lengths of about 100 nm for the iodide perovskite and a stunning 1 μm for the mixed halide perovskite.⁸ What makes the materials so good? And how can the devices be made better?

Point defects

Yan and colleagues had been studying the defect physics of other promising thin-film solar-cell materials, such as cadmium telluride and copper indium gallium selenide. Thin films of those materials are full of point defects that create electron energy levels near the middle of the semiconductor bandgap. Charge carriers that encounter those defects can lose energy, and electrons and holes can recombine, both of which hinder device performance. As Yin explains, "Our previous understanding of inorganic solar-cell materials led us to



believe that the halide perovskites must exhibit unusual defect properties."

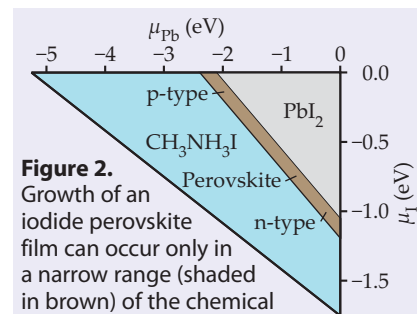
There are only so many ways to make a point defect in a crystalline material: A lattice site can be vacant; an extra, or interstitial, ion can be present between lattice sites; or one ion can take the place of another. Focusing on the iodide perovskite (because the locations of I and Cl in the mixed-halide perovskite aren't completely known), the researchers systematically looked at the 12 possible point defects. For each, they sought to calculate both the defect's formation energy and the electronic energy levels that it creates.

The formation energy of a defect depends on the chemical potential μ of each of the constituent ions during film growth; the chemical potential depends in turn on the ion's concentration or partial pressure. Stable growth of the iodide perovskite means that the chemical potentials of its constituent ions add up to the formation energy of the perovskite, so once two of the chemical potentials are specified, the third is known. Furthermore, large swaths of the chemical potential space shown in figure 2 are excluded because another phase—either PbI_2 or $\text{CH}_3\text{NH}_3\text{I}$ —forms before the perovskite does. That leaves a narrow, effectively one-dimensional range of perovskite growth conditions.

Yan and colleagues did their defect calculations at several points along that range. They found that wherever they looked, all the readily formed defects—such as Pb vacancies or interstitial methylammonium ions—created states with energies at the edges of the bandgap. Defects that create states near the mid-

dle of the bandgap—such as interstitial Pb ions or one ion substituting for another of the opposite charge—all had prohibitively high formation energies.

That's an unusual coincidence among materials, but it offers an explanation for why the perovskites can conduct so well even when they're riddled with defects. And based on what's already known about perovskite conductivity, the result wasn't unexpected. More surprising, though, was the finding that at one end of the range of formation conditions, all the readily formed defects produced states at the bottom of the bandgap, and at the other end, all the readily formed defects produced states at the top of the bandgap. That is, depending on formation conditions, the perovskite can have either p-type or n-type conductivity. If that variation can be better harnessed, it could pave the way for new device designs.



Weathering the elements

As perovskites continue on their meteoric rise, several challenges remain. Foremost among them is the stability of the cells. Good solar cells need to last for decades, even as they're exposed to harsh weather conditions. But the perovskites sublime at relatively low temperatures and dissolve in water. Although the cells are sealed against rain-

fall, they can leak. That not only damages the cell but introduces toxic lead into the environment. Some researchers are looking for similarly effective materials that replace the lead with the less harmful tin.

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Nanoscale ordering from bulk processing

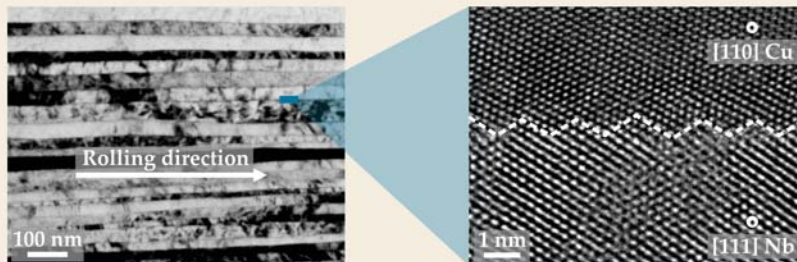
When a metal is forged, stamped, or otherwise strained, it hardens. The change in mechanical properties arises from dislocations in the crystal lattice that enable adjacent planes of atoms to slide past each other. As the metal is worked, the dislocations accommodate the strain; but in doing so, they become entangled, pile up at existing grain boundaries, and produce countless new ones that impede the dislocations' movement and make the metal harder to deform.

For decades, materials scientists have known that nanostructuring a metal—deforming it plastically until the grains shrink to submicron dimensions—can increase its yield strength by as much as an order of magnitude. But many of the newly formed interfaces are unstable: In the harsh environment of a hot jet engine, say, or an irradiating nuclear reactor, grains can grow larger or become decorated by voids due to the agglomeration of lattice vacancies. In either case, the metal loses strength.

The stability of an interface is closely tied to how ordered it is; the greater the order, the lower its formation energy. Epitaxial vapor deposition and other near-equilibrium growth techniques are known to produce nearly perfectly ordered films, layer by layer, from chemically immiscible metals. In addition to their high strength—interfaces between the different metals are even more effective obstacles to dislocation movement than are grain boundaries—such heterostructures possess extraordinary thermal stability and radiation tolerance. Unfortunately, vapor-deposition techniques are limited to thin films and coatings and are not scalable to the bulk materials used in engines, reactors, armor, and the like.

Irene Beyerlein and her colleagues at Los Alamos National Laboratory have now shown that a simple bulk processing method can produce similarly stable and ordered interfaces, provided enough strain is applied.¹ Their method could hardly be more straightforward. By subjecting an alternating stack of millimeter-thick copper and niobium sheets to a metalworking technique known as accumulative roll bonding—repeatedly rolling the sheets thin and then cutting and restacking them like croissant dough—the researchers reduced the layers of Cu and Nb to as thin as 20 nm, as shown in the figure. That's equivalent to stretching a nickel coin to a length of 2.2 km.

Astonishingly, at such enormous strain, all the bimetallic interfaces took on the same low-energy zigzag structure, with nearly defect-free layers of Cu and Nb on opposite sides. Says Beyerlein, "No materials scientist would have expected that, based on our current understanding of interface evolution." Using neutron diffraction, the researchers measured the bimetal's texture—its distribution of crystallographic orientations—after several stages of the plastic deformation. When the layers became



thinner than about 700 nm, the texture changed sharply and only one crystallographic orientation emerged from the relatively large number (roughly 25) of orientations prevalent above that thickness. The result stands in stark contrast to the several orientations that are stable in Cu or Nb when rolled alone.

Cutting open the bimetal laminate, the Los Alamos researchers examined several interfaces using transmission electron microscopy, which explicitly revealed their uniformity. The group's molecular dynamics simulations later explained it: The emergent orientation corresponds to one of the minima in the interface formation-energy landscape of the material. Only one orientation actually survives the strain of deformation because it must do more than just closely align the natural facets of the Cu and Nb planes being joined. It must also not change as the two metals rotate and stretch together along independent slip planes while being squeezed into more interfacial area.

The two stability criteria, Beyerlein argues, offer a powerful paradigm for predicting the favored interfaces that are likely to emerge in other metallic laminates besides Cu-Nb. What's more, the criteria can be applied to other strain paths—say, rolling across the layers instead of along them—and used to predict which interface emerges in response to the change and how that, in turn, influences the mechanical properties of the composite.² As she puts it, "Altering the deformation pathway can be used to tune the atomic structure of the interfaces and thus engineer different kinds of stable materials—that's where we want to take this."

So far, her group has made meter-long, millimeter-thick sheets of the Cu-Nb laminate. Characterization tests have found that the material maintains its hardness of about 4 GPa up to 500 °C; by contrast, the hardness of nanocrystalline Cu (1.8 GPa at room temperature) drops by 66% if heated so much. Also unlike Cu, the composite doesn't develop damaging voids when irradiated with ions. And it remains remarkably ductile, a property usually lost in work-hardened metals.

Mark Wilson

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