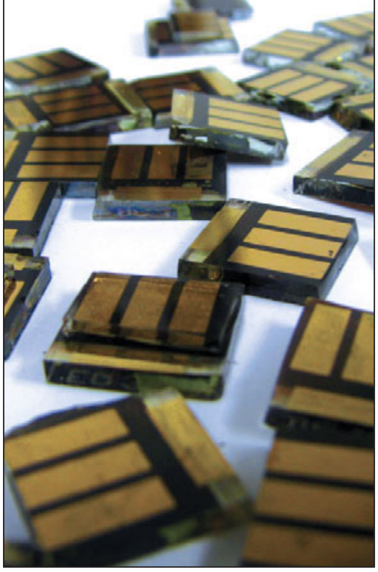

Early studies indicate minimal concern regarding lead in metal halide perovskites, but there is a need for more detailed long-term studies.

Perovskites: Is there a reason for concern?

By **Prachi Patel**
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Perovskites have recently taken the photovoltaic research world by storm. The materials promise solar cells that deliver highest possible efficiencies at lowest possible cost. In the three years leading to 2015, confirmed efficiency claims have passed 20%, with more room for improvement. Silicon solar cells took decades to make that climb.

Their unprecedented PV performance has put perovskites in the limelight. But perovskites are an old material family known for over a century. The term stands for any natural or synthesized compound with the crystal structure of calcium titanate and the chemical formula ABX_3. Hundreds of materials adopt this structure, and they have a variety of properties, including semiconducting, piezoelectric, and thermoelectric.

Oxford Photovoltaics, a UK start-up, says that perovskite solar cells could be on the market by 2017. The use of perovskite materials could soar in the next decade. And not just for solar. The most widely used piezoelectric material for sensors and actuators is the ceramic perovskite lead zirconate titanate (PZT), and its market is escalating, thanks to the advanced engineering of its properties and an ever-larger use of sensors in the automotive industry and in medical and other electronics.

With this increasing use comes a concern for safety. Most commonly used perovskites contain the well-known toxin lead; methylammonium lead iodide is the material of choice for solar cells. Yet, peer-reviewed literature on the potential toxicity of perovskites and their behavior in biological systems or the environment is rare.

"You have a toxic element like lead, and studies haven't been performed yet on what the problems can be, so of course you have to be concerned," said Michael McGehee, professor of materials science and engineering at Stanford University. "There is a very small chance that a panel would leak. It's probably not a show stopper. But on the other hand, I wouldn't say there are no concerns at all and we shouldn't worry about it."

A consortium of experts within the four-year European Union-funded FutureNanoNeeds project is now investigating the health risks and dangers of lead-based perovskite materials. The team, led by Michael Graetzel at the Swiss Federal Institute of Technology in Lausanne, is studying every possible scenario through which perovskite nanomaterials could enter the soil and groundwater, reach the food chain, and affect biological systems. "It's a question of diligence," said Kenneth Dawson, the director of the Center for BioNano Interactions in Ireland who is coordinating FutureNanoNeeds. "The amount of lead in a solar panel is very, very small, mind you. But what if it lays around for decades and the lead washes out?"

So far, though, perovskites are not a top priority on the list of materials to examine, he added, because they haven't raised any alarms.

According to the Piezo Institute, the European hub for research in piezo technologies, the lead in PZT is chemically bound within its crystalline structure, and there is no evidence that it can leach out into the environment. This has permitted many industrial sectors to continue using PZT despite initiatives such as the Restriction of Hazardous Substances in Electrical and Electronic Equipment, which restrict the use of lead and have been adopted by several European countries.

When it comes to perovskite solar cells, some researchers draw the parallel to commercial cadmium telluride thin-film solar cells. Cadmium is a toxic heavy metal, but CdTe cells are proof that PV technology containing a toxic element can be made robust, McGehee said. The crucial difference is that perovskites are unstable, and the lead in them is 14 orders of magnitude more water-soluble than the cadmium in CdTe cells.

Gary Hodes and David Cahen of the Weizmann Institute of Science conducted the first study of the possible environmental effects of perovskite solar cells. They simulated a worst-case scenario in which the methylammonium lead iodide in a damaged solar cell was completely exposed to rain, which was simulated by water of varying pH values. Their experiments showed that rain would rinse out essentially all the lead in the perovskite layer. The impact of that leakage on the ground underneath the solar panel, however, was not shattering.

Researchers estimate that a $1 m^2$ solar panel with a 300-nm-thick $CH_3NH_3PbI_3$ layer would contain about 0.4 g of lead.

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In soil with an average density of 1.5 g/mL, this would increase the lead concentration in the first cm of ground below the panel to around 70 ppm. Typical lead levels in soil are 10–30 ppm for uncontaminated soil and 50−200 ppm or even higher in urban areas.

"I think the major concern [with lead-based perovskites] is psychological," Hodes said. "The amount of lead that gets into the soil is not catastrophic. It ups the background of lead considerably, but it's still within a background limit. Even if you have a huge field of these cells and it all gets into the soil, most of it will stick to the top of the soil in general. It won't go down very far, and will certainly get much weaker as it goes down."

Thin-film solar panel-maker First Solar has a voluntary buyback program for its modules, which contain toxic cadmium. Something similar could be envisioned for lead-containing perovskite solar panels. Credit: Walmart Corporation.

It might be possible to keep the lead in perovskite solar cells from reaching the soil by more robustly sealing and encapsulating the solar cell, covering the ground underneath solar panels with plastic sheets, or applying sodium sulfide to broken solar cells to convert the lead to insoluble lead sulfide.

Identifying lead-free alternatives will also be important. "If you can get rid of anything that's even potentially undesirable, that's good," Dawson said. "And if the alternatives are sensible, practical, and not cost-prohibitive, then why burden a new technology with something it doesn't need to deal with."

Potassium sodium niobate (KNN)-based perovskite ceramics are promising lead-free replacements for the piezoelectric industry. Andrea De Vizcaya-Ruiz and Luz M. Del Razo at the National Polytechnic Institute in Mexico and their colleagues have studied bismuth-based perovskite-structured materials (BNT-BT, which is (0.94) $Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$) as a PZT substitute.

Several research groups are looking at potential replacements for lead-based perovskites for solar cells. Tin is one potential substitute for lead in perovskites. Research groups at the University of Oxford and Northwestern University have made methylammonium tin iodide solar cells. But so far, these have much lower stability and a third of the efficiency of their lead counterparts.

David Mitzi, professor of mechanical engineering and materials science at Duke University, said that lead has some special characteristics for photovoltaics, such as the existence of a lone pair of electrons and the fact that it's a very heavy, polarizable atom. "But it's not unique," he said. "There are other atoms that have lone pairs and that are heavy and polarizable and can make ferroelectric-type compounds. So I believe, in principle, it should be possible to replace lead with other cations, other metals."

It might be early yet to draw big conclusions about the toxicological effects of lead-containing perovskite-based devices. Scientists still need to gather more evidence. Until then, one approach might be to find responsible routes to device disposal. First Solar, the manufacturer of CdTe panels, for instance, runs a reclamation program to take back modules and recycle them at the end of their life. "We could follow the same path if we were to use lead in solar cells," Mitzi said. "I don't know if it's as readily doable as cadmium, but I imagine that it would be." □