

Researchers at the Weizmann Institute of Science in Israel have unveiled how perovskite single crystals heal themselves.

A team led by Davide Raffaele Ceratti, Gary Hodes, and David Cahen used high-power laser light to create small micrometers-wide damaged spots inside crystals of methylammonium, formamidinium, and cesium

lead bromide (MAPbBr₃, FAPbBr₃, and CsPbBr₃).

They measured the photoluminescence of the samples before and after damage. Self-healing occurs in all three materials, they found. Photoluminescence recovered within an hour for MAPbBr₃ and FAPbBr₃, but took tens of hours for CsPbBr₃.

The researchers suggest possible mechanisms for self-healing in their

Advanced Materials (doi:10.1002/adma.20170627) paper. The Weizmann researchers show that the self-healing property of these materials could be due to a closed chemical cycle where degradation products such as ABr, PbBr₂, ABr₃, and Pb(0) can form due to the interaction of APbBr₃ with light, which eventually combine in dark and revert to the original perovskite, APbBr₃.

The use of lead in perovskite solar cells is a bottleneck to their commercial use. Researchers have put a lot of effort into developing lead-free alternatives. Now, researchers in China report antimony-based perovskite-like materials for solar cells that have efficiencies of over 2%, they write in a paper published in the *Journal of the American Chemical Society*. The key is to add a substantial

amount of chlorine into methylammonium antimony iodide (MA₃Sb₂I₉) perovskites to give high-quality films.

In general, MA₃Sb₂X₉ films are made of either octahedral clusters or a two-dimensional (2D) layered structure. The cluster-based structure requires less energy to form, so it is easier to synthesize. The 2D phase, meanwhile, has a bandgap and carrier transport that is more suited

for solar cells, but high-quality 2D layered films have been hard to make.

Lijun Zhang at Huazhong University of Science & Technology, Yinhua Zhou of Jilin University, and their colleagues found that increasing the Cl content by adding MA₃Cl into the mixture of SbI₃ and MAI gives MA₃Sb₂Cl_xI_{9-x} perovskites triggers a transformation from the octahedral cluster phase to the 2D phase.

One critical challenge facing today's perovskite solar cells is the need for hole-transporting materials (HTMs) that are affordable, can be printed using non-toxic solvents, and do not degrade the devices over time.

European researchers have taken an important step toward such market-ready solar cells. They have made a reliable HTM that is easily processed from solution and promises efficient,

stable, and low-cost devices. The research team led by Yi Hou and Christoph Brabec of the Friedrich-Alexander-Universität Erlangen-Nürnberg in Germany developed a two-layer hole-extraction contact made of tantalum-doped tungsten oxide and a polythiophene derivative, poly[5,5'-bis(2-butyloctyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-alt-5,5'-2,2'-bithiophene].

They made solar cells by depositing an ultrathin fullerene-phosphonic acid layer as an electron-transporting material and then the hole-transporting bilayer.

The cells had a maximum power efficiency of 21.2%, the highest yet for perovskite cells with ionic dopant-free HTMs, and were stable for more than 1000 hours, the researchers report in the journal *Science*.

Snapshots of an oxide heterojunction reveal an interfacial atomic shuffle

The design and synthesis of functional oxide interfaces with desirable properties is currently limited by gaps in our understanding of growth pathways at the atomic level, as well as a lack of precise methods to control growth dynamics. LaFeO₃/SrTiO₃ heterojunctions, which are of great interest for photocatalytic water splitting, provide a case in point; groups using different growth methods and characterization tools have reported conflicting results. Now, a research

team at Pacific Northwest National Laboratory (PNNL) in Richland, Wash., has taken a step forward with its use of shuttered molecular beam epitaxy, electron energy-loss spectroscopy, and *ab initio* simulations to explore the structure and dynamics of interface synthesis.

"Our work illustrates the importance of carefully controlling the quantity and arrival time of the atoms introduced to a growing film. By using a shuttered growth mode, we can coax the system into new, previously untapped structural configurations. These results will have widespread application to the growth of all oxide thin films," says lead author Steven Spurgeon. The work was reported in a recent issue of

Physical Review Materials (doi:10.1103/PhysRevMaterials.1.063401).

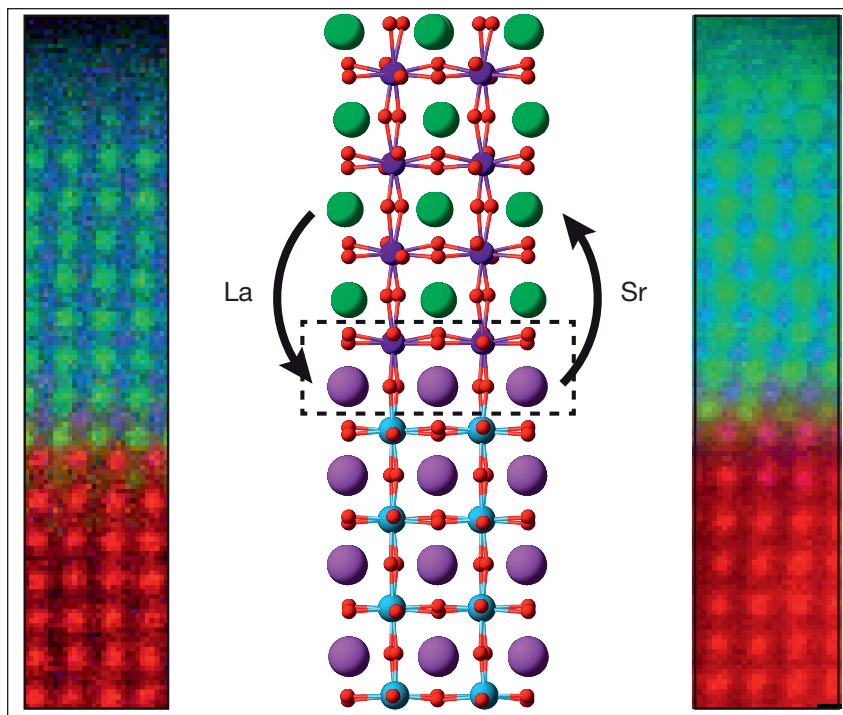
As compounds with perovskite ABO₃ structures, the surfaces of the LaFeO₃ and SrTiO₃ compounds can take on more than one atomic configuration. For example, the (001) SrTiO₃ surface can present either a SrO or TiO₂ layer, which can be controlled by pretreating the substrate. At the heterojunction, the matching LaFeO₃ terminations would be either FeO₂ or LaO, resulting in FeO₂/SrO and LaO/TiO₂ interfaces, respectively. But nothing is ever perfect, so defects such as misfit strain, oxygen vacancies, cation intermixing, and even the migration of entire lattice planes have

been identified as potential influences on the structure and properties of oxide interfaces. The PNNL team launched its investigation with an eye toward examining the factors that influence the stability of heterojunctions. They hoped to gain insight into how growth modes can lead to different synthesis outcomes, as well as reconcile the conflicting results of previous $\text{LaFeO}_3/\text{SrTiO}_3$ heterojunction experiments.

As their growth technique, the researchers chose shuttered oxygen molecular beam epitaxy (MBE) in preference to other techniques like pulsed laser deposition (PLD). In PLD, all species are ablated simultaneously from a stoichiometric sintered target, whereas MBE permits control over the flux of each species independently by opening and closing a shutter on pure elemental sources, yielding more granular control of the deposition process. In their experiments, SrTiO_3 served as the substrate with a TiO_2 termination. Depositing a single layer of SrO produced the alternative termination. Layers of LaFeO_3 were then grown on these substrates in a shuttered growth sequence. For example, LaO was deposited on the TiO_2 surface followed by a layer of FeO_2 and the sequence repeated until a nine-unit-cells-thick LaFeO_3 layer was obtained, and FeO_2 was deposited on the SrO surface followed by a layer of LaO and repeated for nine unit cells.

The PNNL team used aberration-corrected scanning transmission electron microscopy and electron energy-loss spectroscopy (STEM-EELS) as its primary characterization tool. “STEM-EELS allows us to simultaneously investigate structure, chemistry, and composition at near unit-cell level resolution,” Spurgeon says. What they found was that the interface was predominantly LaO/TiO_2 with a stacking sequence $\text{FeO}_2/\text{LaO}/\text{TiO}_2/\text{SrO}$, regardless of the termination of the SrTiO_3 substrate before LaFeO_3 growth. While their composition maps revealed some intermixing on each side of the interface, there were no obvious chemical state changes that could suggest a mechanism for interfacial reconstruction.

To explain these findings, the team turned to *ab initio* density functional



Oxide interface reconfiguration. Scanning transmission electron microscopy–electron energy-loss spectroscopy (STEM-EELS) composition maps of LaFeO_3 grown on SrTiO_3 with a SrO termination (left) and that of LaFeO_3 grown on a SrTiO_3 substrate with a TiO_2 termination (right) are nearly identical and show that both have LaO/TiO_2 interfaces. (Center) Illustration showing how the exchange of lanthanum and strontium atoms across the interface (dashed box) could induce the observed transformation of the FeO_2/SrO interface. Green = lanthanum, magenta = strontium, blue = iron, cyan = titanium, and red = oxygen atoms. Credit: Steven Spurgeon, Pacific Northwest National Laboratory.

theory simulations. “In our simulations, we are able to quickly survey a variety of growth parameters to identify mechanisms that operate in different regimes,” Spurgeon explains. “In this regard, *ab initio* lends strong support to our experimental observations.” The first step was to examine the stability of the two interfacial configurations expected when LaFeO_3 is grown on the two types of SrTiO_3 terminations. Consistent with their experimental observations and a wide body of literature showing that the TiO_2 termination is easier to stabilize, the simulations revealed that the FeO_2/SrO interface is less stable than the LaO/TiO_2 interface for the chosen growth conditions.

Why is the LaO/TiO_2 interface more stable than the FeO_2/SrO interface? According to the simulations, the key lies in the first film layer deposited on the substrate. Deposition of lanthanum leads to an ordered, stoichiometric

configuration. However, under the experimental conditions, iron deposition results in a Fe_2O_3 plane with oxygen vacancies that can enable cation movement. This instability can ultimately convert the interface to an entirely different structure through a process called dynamic layer rearrangement. The PNNL team’s simulations showed that this rearrangement can occur through several pathways, most likely the exchange of lanthanum and strontium atoms.

Spurgeon sums up, “Understanding growth dynamics will help us more precisely control and engineer the band offset in the $\text{LaFeO}_3/\text{SrTiO}_3$ system, which in turn will give us better control over electron–hole pair behavior in photoactive devices. Our group also plans to explore dynamic control of flux in more detail to see what other interesting interface configurations and structures we can unlock.”

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