

## PEROVSKITE SOLAR CELLS

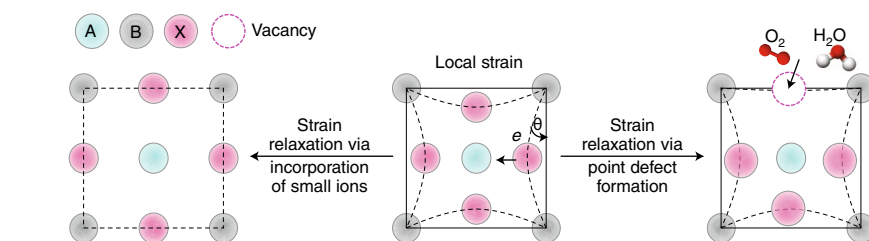
## More stable when relaxed

Perovskite solar cells are noted for their high performance and ease of synthesis, but are still plagued by concerns over their stability. Researchers are now demonstrating why higher performance and increased stability go hand-in-hand — and how to continue improving both.

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Over the past eight years, organic–inorganic (or ‘hybrid’) metal halide perovskites have flouted conventional solar cell wisdom by satisfying a wish-list of criteria for light-absorber materials: they absorb light over a range of wavelengths that can be tuned to encompass the highest number of high-energy photons available from the sun; the photoexcited electrons remain in an excited state long enough to be extracted and perform work in an external circuit; and they can be synthesized by simple, low-energy, wet-chemical (that is, solvent-based) techniques. However, they continue to exhibit a critical Achilles heel: a marked instability towards heat and atmospheric moisture. Writing in *Nature Energy*, Maksud Saidaminov, Edward Sargent and colleagues at the University of Toronto provide experimental and computational tests of the hypothesis that instability towards moisture ultimately stems from defects caused by strain in the perovskite crystal lattice; further, they demonstrate how partially substituting large ions in the structure with smaller ones can relax lattice strain and significantly enhance the material’s stability and performance<sup>1</sup>.

The term ‘hybrid’ in the context of hybrid metal halide perovskites refers to the unusual composition of these materials. They are described by the formula  $ABX_3$ , where  $BX_3$  represents a metal halide component (for example,  $PbI_3$ ), comprising the inorganic portion, and A represents not an elemental ion, but rather an organic molecular cation, such as formamidinium ( $HC(NH_2)_2^+$ , abbreviated FA). Hybrid is also an apt term for the exotic physical properties of these materials, which combine the precise, long-range order of crystalline materials with the extremely dynamic motion and facile structural equilibration typical of soft matter<sup>2</sup>. One consequence of this soft, dynamic behaviour is that structural rearrangements that reduce the energy of the system readily occur. Consider, for example, the influence of inherent strain, that is, non-ideal bond distances or angles, enforced by the



**Fig. 1 | Effects of strain in perovskite structures.** Local strain inherent in  $ABX_3$  materials can be relieved by either compositional engineering or by spontaneous, unwanted defect formation. Substitution of  $Pb^{2+}$  with small cations such as  $Cd^{2+}$  relieves strain that would otherwise be relieved through defect formation. Ultimately, defects lead to poor solar cell performance and phase instability, assisted by moisture.  $e$ , electrostatic force;  $\theta$ , distortion force. Reproduced from ref. <sup>1</sup>, Springer Nature Ltd.

structure of the crystallographic unit cell. The formamidinium lead iodide (FAPbI<sub>3</sub>) perovskite is an inherently strained structure at ambient temperature, and its dynamic nature facilitates the spontaneous rearrangement to a non-functional, non-perovskite phase to relieve this strain — especially in the presence of even trace amounts of moisture. A material so acutely sensitive to environmental conditions would be utterly inappropriate for deployment in a solar cell.

It was recently discovered that this instability is partly ameliorated in perovskites by partially substituting smaller cations and anions into the A- and X-sites, respectively. Critically for device applications, this ion substitution has the fortuitous consequence of simultaneously improving the electronic performance of these materials<sup>3–5</sup>. Through a combination of hypothesis-driven choices and Edisonian optimization, researchers arrived at moderately stable and high-performance perovskite solar cells with complex mixtures, consisting of as many as three distinct cations at the A-site, with simultaneous mixing at the X-site. Both simple arguments<sup>6</sup> and more complete theories<sup>7</sup> offer explanations to why such mixtures might be more stable towards phase change. The work of Saidaminov, Sargent and co-workers sheds light on why stability and performance

are correlated, and provides new pathways to further improve both.

Until now, a central question remained: why would mixed-ion materials exhibit even greater charge-carrier lifetimes and power conversion efficiencies than their parent phases? Saidaminov, Sargent and co-workers suggest an answer to this by focusing on a mechanism that relieves inherent lattice strain while leaving the phase intact: the formation of a small density of vacancies — sites in which an atom or atoms are missing in the crystal (see Fig. 1). Through density functional theory calculations, the researchers show how the formation energy of these vacancies is significantly increased in the mixed perovskites, indicating a drop in the equilibrium density of such defects from  $10^{17} \text{ cm}^{-3}$  in the pure phase to as low as  $10^8 \text{ cm}^{-3}$  in the mixed phase. The causal role played by strain is then tested by applying an isotropic tensile strain computationally: artificial strain mirrors the relief provided by substituting in small ions, resulting in a similar decrease in the favourability of vacancy formation.

The researchers then undertake photoluminescence lifetime measurements. These experiments demonstrate significantly longer excited-state lifetimes in the mixed phase, supporting the conclusion of reduced defect formation. What makes the experiment most convincing is the fact that

the research team compares single crystals of the two materials, rather than the more-typically studied polycrystalline thin films, eliminating the alternative explanations for differences based on microstructure. The connection between defect reduction and stability is then made clear, as defects are known to form locations for moisture-assisted phase change.

Armed with a mechanistic understanding of how strain reduction influences both stability and lifetime, the authors looked beyond A- and X-site substitution, and considered metals that, when incorporated at the B-site, would further reduce the inherent strain. To demonstrate relevance to devices, the researchers shifted focus to thin films rather than single crystals, in which they showed both further enhancement in photoluminescence lifetime and stability when cadmium is incorporated at the B-site. Again, density functional theory evinces a decrease in strain and an increase in vacancy formation energy. Finally, Saidaminov, Sargent and colleagues fabricate highly-stable solar cells with power conversion efficiency above 20%

using this complex A-, B- and X-site multi-substituted mixture.

This work offers a fresh perspective on the extremely actively studied perovskites. Solid-state materials synthesized by low-temperature, solution-based processes seldom resemble the structural and chemical perfection found in the highly refined, crystalline semiconductor materials typically used for solar cells. Much of the excitement around perovskites has been about their impressive tolerance for the seemingly inevitable defects of low-temperature processing — the excited lifetime of charge carriers is much less sensitive to structural and compositional defects compared to traditional materials. In light of the present study, a contrasting advantage comes into focus: their facile structural equilibration allows them to effectively exclude defects when equilibrium disfavors them. Engineering the composition tilts the equilibrium away from defect formation, and low barriers to rearrangement allow the equilibrium state to prevail. Even a defect-tolerant material benefits from fewer defects. Additionally, this study motivates

new experiments to help understand how strain influences defect formation and how ion substitution interacts with strain. It is a simple matter to apply a strain in a calculation, but with few exceptions<sup>8</sup> the functional consequences of externally imposed strain have not been measured. It is the ability to predict and subsequently test the effect of a perturbation that is the true hallmark of scientific understanding. □

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