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Preview

Routes toward Long-Term Stability of Mixed-Halide Perovskites

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In the recent anniversary issue of *Trends in Chemistry*, Brennan et al. review halide segregation in mixed-halide perovskites, discussing multiple perspectives on the underlying origins and reported routes to retard halide segregation. Here, we argue that only slowing down the segregation may be insufficient to achieve long-term stability.

Halide perovskite semiconductors have recently emerged as alternative materials to well-established semiconductors for several applications, such as solar cells, radiation detectors, lasers, and light-emitting diodes. The enormous research interest is related to their combination of easy processability and excellent optoelectronic properties as well as their compositional flexibility, which enables tuning of the light-absorption and emission properties. Specifically, mixing different halides, for instance iodide and bromide in MAPb(I_{1-x}Br_x)₃ (MA = methylammonium) results in continuous bandgap tunability between 1.6 and 2.3 eV.¹ Mixing chloride into MAPbBr₃ increases

the bandgap to 3 eV, covering the entire visible spectrum. Therefore, mixed-halide perovskites are considered the most promising candidate for tandem solar cells in combination with silicon, where a bandgap of 1.7 eV ($x \sim 0.2$) is required to achieve maximum power conversion efficiencies, and for other applications such as perovskite/perovskite tandem cells, lighting and displays.

However, a major hurdle for mixed-halide perovskites that needs to be addressed is their instability under illumination or in an electric field. Following the initial report from Hoke et al.,² there have been many studies

showing segregation of halides into domains, for instance iodide- and bromide-rich in the case of MAPb(I_{1-x}Br_x)₃. As a result, charge quickly transfers into the lower-bandgap iodide-rich domains, where it recombines. This effective reduction in bandgap leads to open-circuit voltage (V_{OC}) losses in the corresponding solar cell. In addition, this segregation drastically affects the emission spectrum and hence reduces the color-purity of the LEDs. For any of the applications of mixed-halide perovskites that require stable and color-tunable bandgaps, full suppression of halide segregation is thus essential. Many strategies that lead to improved stability against segregation have been reported in recent years, including variations of the perovskite composition or synthesis route and post-synthetic treatments. In addition, it is widely reported that the stability against segregation depends on the illumination conditions. However, a single rational model that captures all observations is still lacking.

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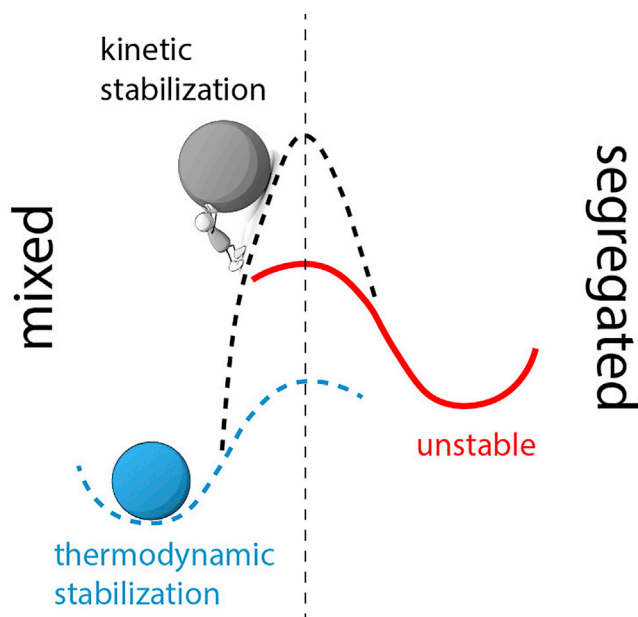


Figure 1. Energy Landscape of Halide Perovskites

In a special anniversary issue of *Trends in Chemistry*, Brennan et al.³ review the existing literature on halide segregation in mixed-halide perovskites. First, they provide an overview of the influence of halide segregation on the structural and optical properties of mixed-halide perovskites. This is followed by an extensive discussion on the kinetics of segregation. Segregation rates are usually determined from the time-dependent ingrowth of the iodide-rich emission peak during illumination, and the authors discuss the interdependency between the illumination conditions (i.e., wavelength, intensity, and duty cycle) and the segregation rate. They note that the activation energy for halide segregation (0.28 eV) matches well with the activation energy E_A for ion migration, suggesting vacancy-mediated anion transport. In addition, Brennan et al. emphasize the presence of an excitation intensity threshold: no segregation is observed at charge densities below $\sim 5 \times 10^{10} \text{ cm}^{-3}$. From this perspective, they critically assess previous work in which segregation rates were found to vary with layer thickness and excitation energy. Finally, the review divides the previously proposed driving forces for

halide segregation into three categories: thermodynamics (1), polaron-induced (2) and electric fields due to trapped charges (3). They note that none of these models captures all previous observations and conclude that a definitive model is thus still lacking. Finally, the review highlights the interesting but poorly understood observation that the segregated iodide-rich phase always corresponds to $x \sim 0.2$, independent of the initial composition (for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$). Halide segregation is absent if $x < 0.2$. As an empirical rationalization, this terminal x -value has been related to the tetragonal-to-cubic phase transition, which also occurs at $x \sim 0.2$. The x -values corresponding to the tetragonal-to-cubic phase transition will likely shift with temperature and pressure. Therefore, to conclusively determine whether this phase transition is indeed responsible for the terminal x -value, we suggest a combination of XRD and optical measurements as a function of temperature or pressure.

The review by Brennan et al. provides an excellent overview of previous studies on halide segregation and lists several directions for future research.

Sorting the segregation mechanisms proposed into three categories is interesting and useful. In our opinion, the three reported categories are not mutually exclusive, and instead the stability of mixed-halide perovskites is affected by both kinetics and thermodynamics (Figure 1). We therefore suggest that future research should focus on obtaining a deeper understanding which factors govern the thermodynamic stability and which ones the kinetic stability. For instance, if there would be polaron-induced lattice deformation, how is this expected to change the activation energy (kinetics) and the local volume ($P\Delta V$ term in thermodynamic phase diagram)?⁴ Additionally, how stable are mixed-halide perovskites at solar cell relevant temperatures of up to 90°C ? Do high temperatures lead to entropic stabilization (thermodynamics) or does halide segregation become faster due to the lower $E_A/k_B T$ (kinetics)? And more general, is it feasible to design thermodynamically stable mixed-halide perovskites, or should future endeavors aim at retarding segregation until it is slow enough not to occur during the lifetime of a solar cell or LED (kinetically stable)?

For these applications, both kinetic and thermodynamic stabilization, or even a combination of the two, would provide a route to sufficiently stable mixed-halide perovskites. The V_{OC} of a solar cell scales with the energy of the photo-excited charges. Assuming that after segregation, all charges recombine in the lower-bandgap iodide-rich domains, the V_{OC} reduces by the difference ΔE between the iodide-rich phase (after segregation) and the initial bandgap (before segregation). If the desired mixing ratio x is close to a thermodynamic minimum, then ΔE and thus the reduction in V_{OC} will be small (thermodynamic stabilization). A large ΔE on the other hand, leads to significant losses in the V_{OC} as well as the color purity of an LED. Therefore, if the initial mixing ratio is far away from the iodide-

rich mixing ratio, the rate of degradation will largely depend on the migration timescales of the halide anions (kinetic stabilization). This means that the degradation rate $k_{\text{deg}} \propto D$, where the diffusion coefficient of the halides,

$D = D_0(N_{\text{ion}}) \times e^{\frac{E_A}{k_B T}}$ depends on the density of mobile halides N_{ion} .⁵ In many of the state-of-the-art mixed-halide perovskites, full segregation takes place on timescales of minutes to hours ($1 - 10^2$ minutes). For solar cells, stability on the timescale of 20 years is required (10^7 minutes). Purely kinetic stabilization could thus be achieved by increasing the activation energy by roughly an order of magnitude to around 3 eV or decreasing the mobile ion density by five orders of magnitude to around 10^{10} cm^{-3} .⁶ A combination of the two would of course also be possible, e.g., $E_A \sim 1.5$ eV and $N_{\text{ion}} \sim 10^{12} \text{ cm}^{-3}$. If the entire system could be moved closer to its thermodynamically

stable mixing ratio,⁷ then the requirements on the kinetic stabilization are dramatically relaxed because of the linear dependence of V_{OC} loss on ΔE .

These considerations show that efforts toward bandgap-tunable, stable materials would benefit from a concerted effort to combine thermodynamic and kinetic stabilization against phase segregation in mixed-halide perovskites.

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Preview

Mighty Morphin(g) Amorphous Metals

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It is well established that one weakness of metallic glasses is their characteristic strain softening and resulting sudden failure. In a recent work in the journal *Nature*, Greer, Li and colleagues demonstrate an ingenious method to instill strain hardening into metallic glasses.

I used to tell my undergraduates that metals are defined by their crystalline structure—the atoms like to align and pack in a characteristic way. Indeed, the properties of metals and alloys—both mechanical and transport—are typically dependent on how these structures are ordered and/or deviated from that order. When the atomic arrangement changes orientation, you

get grain boundaries (simply the border between one arrangement and another). Likewise, a few out-of-place atoms (in different configurations) define defects and dislocations. These boundaries, defects, and dislocations can be exploited under mechanical stress—they act as points or bands of resistance during deformation and result a phenomenon called strain-

hardening (this, of course, is a gross simplification).

Strain hardening is a good thing—it gives a warning before failure. If a piece of metal yields (onset of plastic deformation) at a load of, say, 100 floops, and you load it with 101 floops, it is going to strain harden and likely undergo extreme deformation, but it won't fracture; strain hardening results in a little bit more load capacity when you need it (but don't press your luck). What happens if you remove this crystalline ordering?

Carrying out this thought experiment resulted in the advent of *metallic glass*,

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