

Electronic Supporting Information (ESI)

When defects become ‘dynamic’: Halide Perovskites: a new window on Materials?

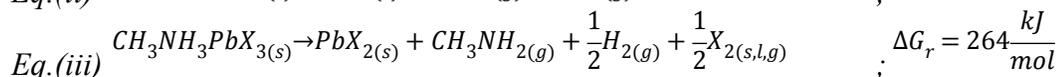
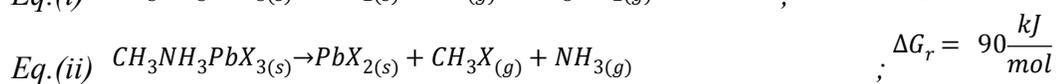
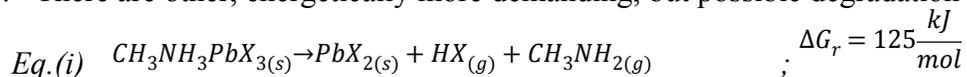
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Footnote comments:

- i. This is in addition to intrinsic properties, such as arrangement of atoms and its symmetry (i.e., structure), and nature of bonding between atoms.
- ii. Formation of defect-pairs, which do not affect the net carrier concentration, is another option. Such doping compensation should manifest itself in a positive, rather than negative, temperature-dependence of the mobility and not only in phonon-scattering dominated regimes.¹ However, if defects cancel or neutralize each other, but still are present in high concentration, this manifests itself in a temperature-independent mobility at low temperatures, which has not (yet) been observed for HaPs.^{2,3}
- iii. In this analysis we use ΔG_r for the material’s free energy of formation in a *reaction from constituents* that are not the elements, but which has the lowest free energy from among other possible constituent combinations and processes. ΔG_f is reserved for *formation from the elements*.
- iv. There are other, energetically more demanding, but possible degradation paths:⁴⁻⁶



ΔG_r refers to MAPbI₃ at 300K.

- v. At 300K, $1 \cdot k_B T \approx 2.5 \text{ kJ/mol} = 26 \text{ meV}$.

- vi. The actual value for S_r ($\sim 350 \frac{\text{J}}{\text{mol} \cdot \text{K}}$)⁵ is very high for what is, based on X-ray and neutron diffraction and optical absorption and emission data, a well-ordered solid and more akin to that of dynamic systems like liquids than to (statically) ordered solids.⁷ The high entropy values can be attributed to the vibrational and configurational degrees of freedom, which clearly are higher here than in ‘classical’ semiconductors.^{8,9} The difference can be ascribed to the higher coordination numbers between atoms in the structure, to which corner-sharing of coordination octahedra, enabling the octahedra to tilt and rotate, should be added. While to some extent HaPs seem similar to polymers, especially proteins, which are also dynamically disordered, proteins lack the static order of the former.⁵

- vii. CuInSe₂ (and possibly other chalcopyrites), like HaPs, is another potential composition with $\Delta G_r \sim (few) \cdot k_B T$ for decomposition to binaries (CuSe₂ and In₂Se₃). Despite the low ΔG_r , the activation energy for ion diffusion in CuInSe₂ is large enough to allow kinetically-stabilized defects, in contrast to the case of HaPs. This point is further discussed later in the main text.
- viii. This range for ΔH_f^{defect} in HaPs fits the range of Shockley defect formation energy in PbBr₂ of V_{Br} ($\Delta H_f^{point} \sim 160$ kJ/mol), the only direct experimental value available (known to us) for Pb-X systems.
- ix. Schottky or Frenkel defect formation energies for stiff materials^{7,10} such as oxide perovskites¹¹ are usually $> 300 \frac{kJ}{mol}$. Solid halides typically have much lower ΔH_f^{defect} ($\sim 70 - 150 \frac{kJ}{mol}$ at room temperature)^{12,7,10} which, to a first approximation, can be explained by the decreased Coulomb lattice (Madelung) energy, which scales with the effective charge on the anion.¹³ Following the similarities in the defect activation energies in Pb-based halides and, because no radioactive isotope tracing studies have as yet been reported for Pb HaPs, $\Delta H_f^{defect}(PbBr_2) \sim 160 \frac{kJ}{mol}$ is the only value that can be used to give an idea of the *point* defect formation energy in HaPs (which is named in Figure 2(ii) as ΔH_f^{defect}).
- x. This relation can be used in the limit where $N_{(sites)} = \frac{N}{a^3} \gg n_{eq}$, which is, generally, true ($\frac{N}{a^3} \sim 2 \cdot 10^{22}$ defect sites).
- xi. The ‘self healing’ experiments were done inside crystals, using 2-photon excitation, i.e., no mass change occurs. 1-photon excitation of the surface resulted in irreversible degradation (more so if the A cation was a volatile organic), because of a driving force for change via the law of mass action.
- xii. From the similarity between the ionic conductivity from impedance and Br-isotope tracer measurements, it was concluded that σ_{ionic} is due to the halide. Impedance analyses on CsPbBr₃ and CuPbBr₃^{14,15} gave E_a for ionic migration (*assumed* by the authors to be Br⁻) very similar to that found via isotope tracer studies in PbBr₂ (Figure 2 (ii)), i.e., 24 and $26 \frac{kJ}{mol}$, respectively. For MAPbI₃, assuming I⁻ migration, $E_a \sim 35 - 41 \frac{kJ}{mol}$.^{16,17} In those studies the authors *assumed* I⁻ migration to dominate.
- xiii. These three points fit the ‘entropy’ concept – a statistically averaged situation, reflecting a collective energy state of a system that a ‘slow’ observer cannot observe.
- xiv. This can be, for example, a surface dipole, as systematically demonstrated by Zohar et al.¹⁸ to affect the Fermi level within an HaP layer. However, doping attempts with Bi³⁺, O₂ or I₂, showed only quite inefficient doping.^{19–21}
- xv. An additional reason is very likely the presence of a heavy element.
- xvi. “Forgiving” deposition processes, like ‘spin-coating’, result in polycrystalline films with high quality bulk material (with low static disorder as evidenced by narrow diffraction peaks).^{22,23} Further evidence

comes from the Urbach energy, E_U , which is small compared to that of other polycrystalline optoelectronic materials,²⁴ and especially, its temperature-independent part, an indicator for static disorder, which is $\sim 60\%$ less than that of high-quality single crystalline Si and GaAs.²⁵ Further discussion on E_U is in the main text.

- xvii. Motivated by the ‘van Arkel-Ketelaar triangle’.²⁶
- xviii. Another possibility is formation of kinetically-stabilized bulky complexes that will require more time or energy to diffuse to the surface/ interfaces (e.g. – complexes with large solvent molecules)²⁷.

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