

Lessons from (lack of) Defects in Halide Perovskites

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While from the device fabrication point of view the low defect density in halide perovskites, is a “gift” that is happily accepted as is, one does wonder how this can be possible. The defect density is remarkably low, especially if we consider the quick and “chimie douce” way in which films as well as of most single crystals can be synthesized.

The densities of electrical defects are all deduced from the common (all indirect) measurements, e.g., space-charge limited current, thermally stimulated current and deep level transient spectroscopy. Optically, the methods that can be used include sub-bandgap absorption via transmission or reflection, photothermal deflection spectroscopy, photoluminescence, external quantum efficiency (spectral response) and surface photovoltage spectroscopy, at times using extra modulation to allow Fourier Transform. Other methods include electron spin resonance, photocurrent and scanning tunneling spectroscopy. All these have been used and more, at times with modeling to fit to one or more defect levels.

The most salient results are that single crystals show 10^9 - 10^{10} cm⁻³ electrically active defect densities, while thin polycrystalline films (all of MAPbI₃ or MABr₃ or mixtures thereof) give 10^{13} - 10^{16} cm⁻³ densities. The difference is likely due to surface and grain boundary effects, even though scanning probe measurements indicate relatively benign grain boundaries. Results from chemical surface treatments of films do show, though, that such treatments can significantly increase the luminescence quantum yields and for nanocrystals of CsPbBr₃ 100% QY has been reported after ligand exchange. EPR experiments mostly do not detect HaP-originated signals. Carrier densities that can be

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estimated, using a most likely mobility value of $10 \text{ cm}^2/\text{Vsec}$, can be as low as 10^{10} cm^{-3} in polycrystalline films.

I intend to show how this behaviour reflects a quite fundamental property of these materials, with a rather simple thermodynamic basis. The key point is the low free energy of reaction of the HaP into its binary constituents. Starting from this calorimetric result (based on data from several groups), one arrives not only at likely entropic stabilization and additional stabilization by mixing different cations on the A site, but at the paradoxical conclusion that the low defect density is directly connected with the low free energy of reaction, low relative to the estimates we can make for the free energies of formation of plausible defects.

Corollaries of this analysis concern the ability to dope these materials extrinsically, self-healing capacity and the importance of the dynamic disorder for the low defect densities.

Potentially, the conclusions can be used to start mining databases for other such materials.

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