Hidden and Questionable Assumptions for Halide Perovskites

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Several times, in Halide Perovskites (HaPs) research ideas were taken as "facts", but with either insufficient experimental evidence or because common assumptions were (are?) used that should at least be questioned in the Pb-HaPs[1] (which I will refer to from now on as HaPs, excluding Sn-based HaPs and double perovskites).

An early example is that of "high" mobilities,[2] which was likely added because of initial excitement and enthusiasm about the treasure chest that was re-discovered. In fact the mobility was OK, enough for a relatively simple device such as a solar cell (it is the $\mu\tau$ product that really counts and τ can be long, although see below about problems in determining it). Amazingly what seemed much less on the radar was the unusual temperature dependence of the carrier mobilities that was already showing itself early on. That dependence actually did show a feature of HaPs being special, namely behaviour that is consistent with a lack of classical defect scattering.

Related to mobilities was the idea of very long diffusion lengths which, in the frame of common photovoltaic cell understanding, at the time, implied minority carrier diffusion lengths.[3] Such high values are then connected with high mobilities, diffusion coefficients and lifetimes. However, the HaPs are remarkable in having so low carrier densities, esp. as single crystals, that the distinction between minority and majority carriers becomes problematic.

Next was (is) *intrinsic* instability. This stemmed from observations of devices or of material (nearly always thin films of < 1 μm grain size) in reactive ambient, suggesting that the concept of surface and hence interface reactivity was not appreciated, even though it is used regularly for semiconductors and some of their properties. Indeed, modern semiconductor technology would not have been possible if the surfaces of the relevant materials had not beern "tamed".

HaP stability is, as is by now pretty well agreed on, first and foremost determined by its surfaces and interfaces.[4]

The issue of "*bulk"* doping was examined in some detail by several colleagues and me recently.[5] There is little question that we can change the net carrier densities inside a HaP film, i.e., the bulk of a grain can well have different net carrier densities before and after some treatment. However, the most obvious reason (use Ockam's razor) for that is that this occurs by way of surface dopants, instead of bulk defects or impurities within the grains.

Then there is "*defect tolerance*", DT, topic of mostly computational theory studies, a critical viewpoint,[6] and reviews (e.g., a very recent one [7]), on which more below.

All those features are central to explain the exceptional optoelectronic properties of HaPs in PV, LEDs and detectors. This talk focuses on the last two "facts", "intrinsic instability and DT, which make other ones at the very least questionable and probably untenable. The first ones went out of fashion about a decade ago.[2] The related topic of carrier lifetime, specifically as deduced from photoluminescence decay, discussed some years back by Thomas Kirchartz at Quantsol (and appeared in print in 2024 [8]), requires much greater care than is usually taken, in terms of cross-sample and laboratory comparisons.

DT in semiconductors means that structural defects do not lead to (opto)electronically active effects. We found first direct experimental evidence for DT in Pb-HaPs[9] and argue that *strong lattice dynamics*[6, 10, 11] in these intrinsically "soft" and polarizable materials *enable eliminating defects (by self-healing of damage, SH* [12]*) and screening/neutralizing electrical effects of remaining ones (DT),* in line with the computational study of defect level dynamics in CsPbBr3, of Cohen et al.[13]

As noted in Quantsol 2023, doping HaPs as done for Si or GaAs, does not work. I will argue that *their low doping results directly from SH+DT.* The default explanation for Pb-HaP doping is via their surfaces & interfaces.[e] This general idea is "turbo-charged" for HaPs, because

*bulk doping is so low (and hard),
*their surfaces are rather defect-poor and
*eliminating (SH) or "disarming" defects (DT) *on* their surfaces is harder than *inside* them.

Thus, in a way (Pb-)halide perovskites are H Kroemer's "*the interface is the device*" on steroids.

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with esp., A. Kahn (Princeton), G. Hodes (Weizmann), D. Egger (TUM), Y Rakita (Ben Gurion U.); + many more

(lots of self-) **References**

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