What Remains Special about Halide Perovskites ?

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After over half a decade years of great excitement, it is starting to dawn on us that Halide Perovskites behave largely as normal (inorganic) electronic solids. This follows the earlier realization that describing their behaviour with concepts from organic electronics and dye-sensitized solar cells is, at least for basic materials properties, unnecessary. What remains remarkable is that they are soft materials *that can have (very) good quality optoelectronic properties, even if made by a fast, low temperature, solution process.* If we can understand the reason(s) behind this, it may be possible to figure out if this is a nasty trick of nature (that Pb is unique?) or if we can generalize to find other materials like these. Here I will present results from group efforts at the Weizmann Institute and with colleagues from elsewhere,^{##} some of which are at Quantsol (and listed as co-authors). The presentation will look at known physical properties of HaPs, compare some of these with those of other materials, and then see what we think is left.

The remarkable optoelectronic conversion (radiative power to electrical power, and to a lesser extent, electrical power to radiative power) efficiencies achieved with devices based on halide perovskites, **HaPs**, with $A^+B^{2+}X^{-3}$ stoichiometry, begs the question *which, if any, basic physicochemical properties of these materials are unusual compared to other optoelectronic materials?* A major reason to ask this question is that at least in some cases materials, made by relatively low-temperature, fast solution chemistry yielded high-performance devices. Such method of synthesis normally yields materials with significant densities of defects, due to imperfect order and far from ideal long-range spatial periodicity. Indeed, that normal result is the reason that, unless further processed, materials that are prepared in this way show defective optoelectronic behaviour and, thus, they are annealed at high temperatures and cooled slowly, or the synthesis is slowed down. Defective behavior should be reflected in the material (and device) properties, but that is now what is found for HaPs. We will first focus on *fundamental structural properties* and enumerate some salient experimental findings on/with HaPs:

- 1. Depending on which halide is on the X site, the A site is occupied by a small organic and/or a large alkali metal cation, *i.e.*, HaPs can be hybrid organic-inorganic materials.
- 2. The sharp X-ray diffraction peaks of the HaPs, which can form fast (< 1 sec) from solution without high temperature anneal, point to a high crystalline order at length scales > (X-ray wavelength-imposed) diffraction limits.
- 3. They are mechanically 3-10 times softer and exhibit several times lower optical phonon energies than those of common inorganic semiconductors (Si, Gas, CdTe).
- 4. HaPs were found to be enthalpically unstable with respect to their binary components, *implying entropic stabilization of the ternary perovskite*.
- 5. HaPs can be spatially anisotropic, *e.g.*, several phases can coexist within one material.
- 6. At least one HaP is ferroelectric at RT, MAPbI₃
- 7. The A cation is disordered dynamically at room temperature (RT) in HaPs.

8. The halides in HaPs show large amplitude displacements, as determined by neutron diffraction, and dynamic disorder in the lead-halide sub-lattice at RT.

From a purely scientific perspective, each of these eight items on its own is not unprecedented, *i.e.*, there are other materials, which show one of these properties, sometimes even combinations of some of them. So, to make progress towards answering the question that we pose, let's look at some of the remarkable *optoelectronic properties* of HaPs:

- a. The optical absorption edges are sharp and the absorption rise is steep with, for Pbbased compounds, small Urbach energies.
- b. Low densities of states at the valence band maximum, unlike Si and GaAs, but similar to Pb-containing compounds.
- c. The recombination rates of photo-generated carriers ae low, esp. the non-radiative ones; this property allows to get respectable carrier lifetimes and diffusion lengths.
- d. Doping appears primarily intrinsic; no success with extrinsic doping was as yet reported.
- e. On the one hand grain boundaries and defects can be, relatively benign, compared to, say, polycrystalline CdTe or Cu(In,Ga)Se₂, and thus allow for high-quality devices despite low-*T* synthesis. On the other hand there is a 3-4 orders of magnitude difference between defect densities, extracted from experiments, for thin polycrystalline films and single crystals
- f. One or more of the intrinsic defects appear to be mobile, which can give the material mixed ionic-electronic conductivity flavour.
- g. Charge carrier mobilities with a $\sim T^{1.5}$ temperature dependence, and orders of magnitude lower values than expected for mechanisms, consistent with this temperature dependence, a combination that seems to defy conventional scattering theories around RT.

Properties a-g can explain the excellent device performances of devices made with HaPs. Still one or more of these can be found these in some semiconductor.

What emerges as the special aspect of HaPs is the *combination of all these properties* within one (class of) material(s). I will present our views on how this combination of properties can come about, to get back to the question of what is still special in the physical and chemical properties of halide perovskites?

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