What remains unexplained about the properties of halide perovskites?

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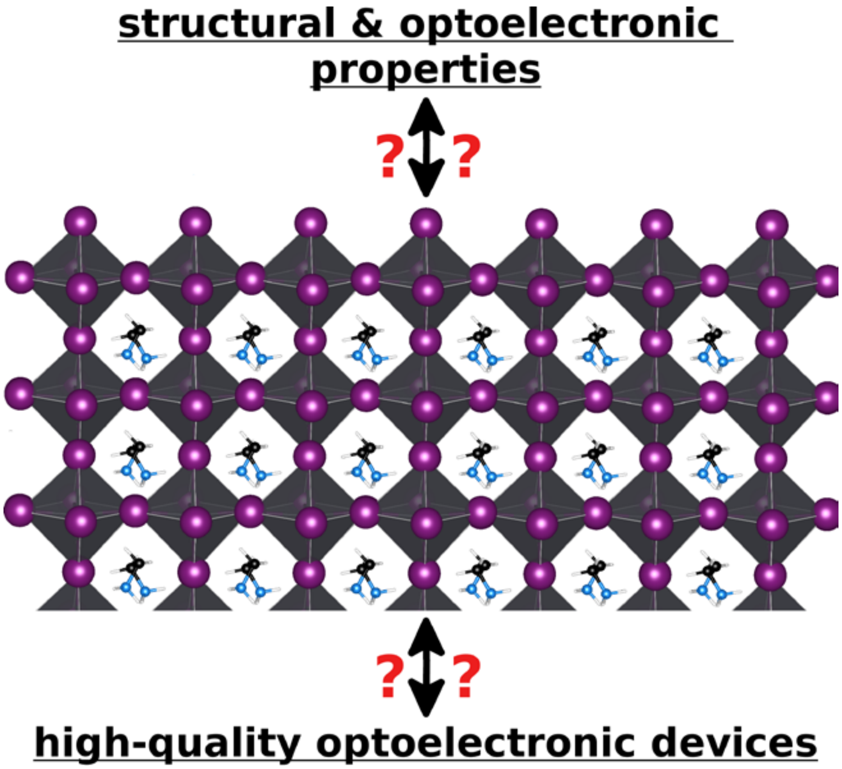
Halide perovskites are fascinating crystalline materials for optoelectronic devices and can yield efficient solar cells. We provide a critical review of their structural and optoelectronic characteristics and find that they exhibit a unique combination of properties. Based on this notion, the Essay addresses open questions about these materials.



Abstract

The notion that halide perovskite crystals (ABX_3, where X is a halide) exhibit unique structural and optoelectronic behavior deserves serious scrutiny. After decades of steady, and half a decade of intense research, we discuss our viewpoint on which attributes of these materials are unusual, with an emphasis on our identification of the most important remaining issues. Our goal is to stimulate discussion, rather than merely to present a community consensus.

Setting the stage The remarkable photovoltaic (PV) conversion efficiencies (radiative power to electrical power) and, to a lesser extent, light emission efficiencies (electrical power to radiative power) achieved with devices based on bulk halide perovskites, HaPs,[1–6] with $A^+ B^{2+} X^-_3$ stoichiometry, prompt us to ask the question: *what is so special about these materials?* A major additional reason to ask this question is that experimental results for actual devices have also been obtained with materials produced by relatively low-temperature solution chemistry. This preparation method may be expected to lead to materials that have imperfect order and a lack of strict long-range spatial periodicity so that, unless further processed, they should exhibit deficient optoelectronic behavior. This should be reflected in both their material and device properties. We therefore start our discussion with a list of experimental facts concerning the *fundamental structural properties* of HaPs, partly visualized in Figure 1:

a. Depending on the halide anion occupying the X site, the A site can be occupied by a small organic and/or a large alkali metal cation, *i.e.*, HaPs can (but do not have to) be *hybrid* organic-inorganic materials with perovskite stoichiometry and structure.[7,8]
b. Notwithstanding the low temperature (T) material preparation method, HaPs show sharp X-ray diffraction peaks (see Figure 1a), indicating a high degree of crystalline order at length scales larger than the (commonly encountered) diffraction limits.[9–11]
c. The crystal lattices of HaPs are 3-10 times softer mechanically and they therefore exhibit optical phonon energies that are significantly lower than what is typically observed in common inorganic semiconductors.[12–15]
d. HaPs exhibit enthalpic instabilities towards decomposition into the binary components,[16] implying entropic stabilization of the ternary perovskites.
e. Despite the high degree of crystalline order mentioned in point b., some HaPs can show spatial anisotropy, *e.g.*, a coexistence of several phases within one material.[17–19]
f. HaPs can be ferroelectric (as are several non-centrosymmetric oxide perovskites), depending on the composition and, of course, temperature.[20–23]
g. The A-site cation in hybrid and all-inorganic HaPs is dynamically disordered at room temperature (RT).[15,24]

h. Consistent with c., the halides in Pb-based HaPs show large amplitude displacements, as determined by neutron diffraction (see Figure 1b),[25] and dynamic disorder in the lead-halide sub-lattice at RT (see Figure 1c).[15,26]

While each item a.-h. by itself is not unprecedented, *i.e.*, there are other materials which individually exhibit one of these properties or sometimes even combinations of them, a system that exhibits all of these properties is already peculiar.

In order to facilitate a discussion between structure and function and to address our title question, we now consider some remarkable *optoelectronic properties of HaPs*, again partly visualized in Figure 1:

i. An electronic band structure showing low effective masses[27,28] (see Figure 1d) and a low density of states (DOS) at the valence band maximum (VBM);[29] the latter is similar to Pb-containing compounds[30] and unlike Si and GaAs, but note that the latter has a relatively low DOS at the conduction band minimum.

j. HaPs can show sharp optical absorption edges and steep optical absorption rise at energies relevant for absorbing solar radiation on earth, with small Urbach energies (for Pb-based compounds), particularly for iodide-based HaPs (see Figure 1e).[31]

k. Low non-radiative recombination rates of photo-generated carriers, which are essential to achieving respectable lifetimes and diffusion lengths, as well as a high open circuit voltage (see Figure 1f).[32,33]

l. Doping in HaPs is achieved primarily by intrinsic (*i.e.*, native) defects, and using extrinsic (foreign dopants) has so far proven to be difficult and showed little success.[34,35]

m. Indications that grain boundaries and defects can be, relatively speaking (compared to, say, polycrystalline CdTe or Cu(In,Ga)Se_2 (CIGS)) benign and thus allow for high-quality devices despite low-temperature (T) synthesis.[36–39]

n. At least one type of mobile ionic defect, which can lead to mixed ionic-electronic conductivity behavior.[40,41]

o. Carrier mobilities, μ, which have a temperature dependence of $\mu \sim T^{-1.5}$,[33,42,43] and a surprisingly low RT magnitude, the combination of which seems to defy conventional carrier scattering theories.[44]

While properties i.-o. may explain the observed outstanding device efficiencies, or are at least related to them, these are again not unprecedented in a more general semiconductor context. However, having reviewed the experimental facts and observations as to the structural and optoelectronic properties, what appears to be very special indeed is the *combination of all properties, a.-o., within one class of materials*. In this Essay, we consider the consequences of this unique combination of properties and how it arises. We address these issues from both a scientific and a technological perspective. Finally, we summarize the properties and observations for which we deem further investigations are important as well as others that appear to be not so special after all, *i.e.*, properties that are known and understood from other PV materials.

Device properties We first note observations that are not unusual if put into the context of other well-studied inorganic semiconductors for high-efficiency solar cells. Firstly, PV cells made with HaPs *can* behave as *ideal p-i-n* diodes,[36,37] which have been modeled by numerical simulations,[45,46] without the need to consider ion movement. Other *p-i-n* devices are well-known,[47] especially a-Si:H solar cells, in which all three components are a-Si:H, or p-AlGaAs/MQW GaAs/AlGaAs/ n-AlGaAs cells.[48] The latter are somewhat closer in structure to that of the HaP cells, in which the HaP acts to a large degree merely as -i-, and the electron- and hole-transporting layers (made of different materials) as n- and p-components, respectively (with likely some part of the HaP adjacent to each of these transport layers, also doped accordingly). This suggests that from a purely device-oriented perspective, HaP-based solar cells are not particularly special as compared to well-established inorganic semiconductors traditionally used in high-quality solar cells.

In addition, the band structure of typical HaPs shows properties known from typical inorganic semiconductors:[5] HaPs have a direct or close-to-direct (displaced by the Rashba effect, discussed below) band gap and low effective carrier masses, see Figure 1d.[27,28,49] Furthermore, the optical absorption coefficient of HaPs, despite the reported low DOS at the VBM,[29] is close to optimal, *i.e.*, an absorption rise that is similarly steep as the one of GaAs (*cf.* Figure 1e) with an Urbach energy at RT (~10 meV for X=Iodide) nearly as small as that of GaAs.[31]

<u>Low-*T* preparation, long lifetimes and benign defects</u> While the device properties discussed above are similar to other well-studied PV platforms, it is unusual that HaPs are often prepared using low-*T* solution chemistry and yet show a device behavior similar to that of devices based on "classical" inorganic PV materials with a sharp optical absorption onset and long charge-carrier lifetimes. Recall that high-quality inorganic PV materials are prepared using at least one high-*T* step. Also, except for thin CdS buffer layers in CdTe or CIGS cells, such materials are made by single crystal growth from the melt or gas phase (c-Si, GaAs), melt-growth (multi- and poly-crystalline Si), vacuum evaporation (CdTe, CIGS), or plasma deposition (a-Si:H).[50] For these established PV materials, prior to their efficient use in devices, the preparation design and conditions had to be optimized over decades of research. For HaPs, building on the lessons learned from previous PV research (including that of organic PV and dye-sensitized cells) progress in device quality was much quicker, and the preparation techniques used for high-efficiency solar cells were much simpler: a very rapid (< 1s) crystallization of HaPs by spin-coating and subsequent short (~minutes), low temperature (< 140 °C) annealing.[51,52] Such a protocol would be expected to produce highly defective materials with correspondingly poor optoelectronic properties and, yet, this is not the case. A finding that may be related to this behavior is the recently demonstrated ability of Pb-bromide HaP single crystals to exhibit a self-healing of the damage caused by moderate to strong illumination.[53]

The slow recombination measured in HaP films is therefore truly outstanding. For example, the lifetimes derived from monomolecular (trap-assisted) decays[33,54] of photoluminescence (PL) or from photoconductivity transients are in the range of hundreds of ns up to several µs,[54] which is obtainable for GaAs only under very special conditions.[55] Furthermore, HaP-based solar cells, once equipped with suitable contact materials, show remarkably high open-circuit voltages relative to the thermodynamic limit of the open-circuit voltage (see Figure 1f).[56,57] Such low losses in photovoltage are intimately linked[58,59] to the high luminescence quantum efficiency, which shows that the luminescence efficiency of the films can be retained in optoelectronic devices. External light-emitting diode (LED) quantum efficiencies reach values of ~1%[60–62], which are outstanding for a thin-film solar cell material.[63] Still, these are just ~1% quantum efficiencies, indicating that further improvements in efficiency are possible by reducing non-radiative recombination, while maintaining the same amount of absorption and radiative recombination. Note that the latter are coupled by the principle of detailed balance, as expressed in the van Roosbroeck-Shockley equation.[64]

The above findings imply that defect properties, which are crucial for the non-radiative lifetime and device performance, must be somehow special in HaP systems, as discussed in several articles over the past few years.[38,53,65–71] In these, concepts such as defect tolerance,[65–68] *i.e.*, the idea that the energy of states due to defects is very close or even within the band edges, and defect healing,[53,68,70,71] *i.e.*, the notion that defects induced during preparation or operation can vanish, were proposed. What exactly underlies the benign character of defects, especially the intrinsic ones in HaPs, and how this is connected to the long lifetimes, is highly interesting scientifically, not well-comprehended fundamentally, and may well be important technologically beyond HaPs.

Role of the organic cation It is interesting to note that PV devices made from HaPs with the non-polar Cs^+ ion behave quite similarly to those with an organic A cation, *e.g.*, using $CH_3NH_3^+$ (methylammonium or MA), or $H_2NC(H)NH_2^+$ (formamidinium or FA) for (3-D) perovskites: the carrier lifetime remains nearly the same and the open circuit voltage is only slightly lower.[72,73] This can be rationalized by the electronic band-structure of HaPs, as the states of the A cation do not contribute to the frontier bands. Thus, one may conclude that the role of the organic cation, at least from a device viewpoint, is not important for the optoelectronic properties and that its sole purpose is structural. Using an organic cation at the A site in combination with Pb^{2+} or Sn^{2+} at the B site and a halide at the X site allows formation of a bulk perovskite structure, *i.e.*, the Goldschmidt tolerance factor is suitable for the crystal to take on the perovskite structure as a stable one. The Pb-halide backbone in the perovskite structure, in turn, provides the electronic structure and optical properties of HaPs, which are then the basis for many of the desirable device-related properties, noted in points i.-o. above. We note that a consequence of the Pb-halide backbone determining the frontier states in the electronic band structure is that similar to Pb-based crystals, but in contrast to Si and GaAs, the band-gap of Pb-based HaPs decreases with T.[74] While the perovskite structure also forms when inorganic A-site cations are used, the organic A-site cation may modify bond-lengths and angles of the inorganic sublattice, which may affect some electronic properties.

A possible experimental indication for this is that the voltage efficiencies of $MAPbBr_3$-based cells are on average ~0.1 eV better than those of $CsPbBr_3$-based ones.[72] Moreover, the choice of A-site cation certainly modulates the details of Raman-active signatures (see Ref. [15] and Figure 1c) and affects phonon speeds and, thereby, mechanical properties,[75] which can be relevant for material stability.[76] There are also different theoretical proposals as to how a polar A-site cation may contribute to ferroelectricity and long carrier lifetimes.[74,77] The mechanistic role of these effects for devices is not fully established, but it is noteworthy that recent advances in "top efficiency" PV cells use HaP alloys with different *combinations* of A-site cations.[60,78] This can be interpreted as a fine-tuning of the Goldschmidt tolerance factor along with Pb-I bond angles and octahedral rotations, which may affect the electronic structure. Another possibility is that the A-site cation may be related to the aforementioned coexistence of different compositions[17,18] and phase segregation[79] in HaPs, by affecting the mechanical stability, grain boundary energetics, and structural fluctuations in these materials. These would likely impact the electronic structure and may therefore be relevant for device properties. However, the role of the A-site cation and its interactions with the environment[80] in these effects is currently unclear.

Ion migration and ferroelectricity Further analyses of the electrical characteristics of HaPs indicate that they can behave as mixed ion-electron semiconductors,[81] with different proposals for which ionic defect is moving.[40] From a materials perspective, ion migration is common for traditional oxide perovskites,[82,83] as are phase segregation[84] and proton conduction.[85,86] Ion migration is also not unprecedented in a PV context, as it occurs in at least one other well-known PV material, CIGS,[87] where it can actually add stability.[88] This is in contrast to the case of Cu_2S/CdS solar cells, which were abandoned because of degradation ascribed, at least in part, to Cu-ion migration.[89,90] Even the fate of the now ubiquitous CdTe/CdS cells was at one point "threatened" by Cu diffusion into CdTe from the Cu-doped carbon back contact.[91] Therefore, while not unique, it is clear that ion migration in HaPs can have a technological impact, considering that it has been implicated in hysteresis of photocurrent-voltage dependence[92,93] and may trigger HaP degradation.

Regarding the hysteresis properties of HaP devices, it is interesting that cells with suppressed hysteresis can be made by tailoring the interfaces,[94–97] *e.g.*, by using a passivating layer. Currently, several proposals for which defect species are mobile are debated,[40,98,99] the most relevant ones being the halide[81,100–102] and MA vacancies[103,104] as well as interstitial proton migration.[105–108] This is because halides and MA are part of the native HaP structure; protons can be present either as intrinsic (formed *via* MA deprotonation) or extrinsic (introduced during synthesis or contact with H_2O) defects.

It has been argued that, depending on ionic composition, HaPs can exhibit ferroelectricity at RT. This was indeed demonstrated for tetragonal $MAPbI_3$ at ~ 200K,[21] but $MAPBr_3$ was found not to be ferroelectric.[20] While ferroelectricity is common for traditional oxide perovskites, it is very rare in the context of mainstream PV and it is not known to occur in commercial PV materials. Even for tetragonal $MAPbI_3$, which is ferroelectric, it is not clear if, and if so how, ferroelectricity affects *its radiative to electrical power conversion at RT*.[21]

Charge-carrier transport For any electronic device, the macroscopic electrical characteristics should ultimately be traceable to the microscopic mechanisms of carrier transport. Here, we encounter a scientific challenge for HaPs. As mentioned above in point o., experimental observations for carrier mobilities have repeatedly shown that, although the calculated and measured effective masses are similar to those of some other well-known inorganic PV materials, the experimental mobilities in HaPs are 1-2 orders of magnitude lower (see Table 1 and Refs. [14,42,43,109–129]). At the same time, the *T*-dependence of the mobility, μ, is similar to that of inorganic PV systems (see Table 1), and around RT follows a power law, $\mu \sim T^x$, where $x \approx -1.5$ for HaPs. This implies that carrier scattering is mainly due to *T*-induced vibrations of the lattice and not due to scattering by (charged) defects, which would yield a positive *T*-dependent exponent for μ.

Technologically, at least for PV devices, the mobility of HaPs is already sufficiently high, as what counts for charge collection is the mobility-lifetime product. Given the long lifetimes of HaPs discussed above, the diffusion length is sufficiently long for good PV efficiencies of a device based on a highly absorptive material, despite the modest μ. Scientifically, it is interesting that when we compare the *T*-dependence of HaPs around RT with that of inorganic semiconductors used in PV devices (see Table 1), we find that these are similar: Si (x=-2.3), GaAs (x=-2.3), CdTe (x=-1.9), etc., and thus the T-dependence of μ is not unusual as such. What is peculiar and not well-understood, however, is that given the low effective masses, and given that the T-dependence of μ is not unusual for typical inorganic semiconductors, why is the RT mobility in HaPs so low?

We suggest that this must be related to the peculiarities of carrier scattering mechanisms in HaPs, *i.e.*, vibrational properties that are not found in other inorganic semiconductors. First attempts to explain the impact of those on charge-transport used well-established scattering theories that were developed for inorganic semiconductors.[130] One such theory invokes deformation potential scattering, which approximates electron-phonon interactions by the change in electronic structure that is induced by long-wavelength acoustic and/or optical phonons.[130] Within this model, using calculated acoustic deformation potential constants,[122,131] mobilities have been derived for HaPs with the result that the T-dependent exponent is correct (x=-1.5), *but RT mobilities are 1-2 orders of magnitude higher than the experimental ones*. To the best of our knowledge, the deformation potential constants corresponding to optical phonons have not been reported for HaPs, and the mobilities derived from this type of scattering are unknown. As HaPs are polar crystals, the long-wavelength longitudinal phonons also create electric fields that can interact with electrons and holes *via* the so-called Fröhlich interaction.[130] This gives rise to large polaron formation, and mobilities according to this type of scattering have been computed for HaPs using the large polaron model.[132,133] *The results are yet again in contradiction to experimental data*, as the large polaron model combined with known material properties of HaPs can yield the right order of magnitude for the RT mobility, but it provides an incorrect T-dependence (x=-0.5).[132–134] Recently, it has been suggested that this apparent contradiction can be resolved by taking the T-dependence of the dielectric constant as well as acoustic phonon scattering of large polarons into account.[135] But the polaron masses calculated in this model are 1-2 orders of magnitude larger than experimentally measured effective electron/hole masses, and compared to experimental RT values of μ this model predicts very low mobilities of ~10 cm^2/Vs at RT.[135]

Thus, it appears that as things stand, traditional models, established for inorganic semiconductors, do not provide a completely acceptable explanation for the vibrational scattering of carriers in HaPs. We therefore advise against forcing these HaPs into conventional “modeling straitjackets” to fit the experimental results. Rather, we think that it is required to go beyond the above-described traditional models to understand microscopically what may well be unusual carrier scattering in HaPs. At the same time, it will be essential to make progress experimentally by, *e.g.*, measuring μ at very low T to look for signs of other scattering mechanisms and to compare the T-dependence of hybrid and all-inorganic HaPs. In this context, it is important to note that in HaP-based transistors, mobilities were measured to be only ~1 cm^2/Vs at RT,[136] and that initial mobility measurements of (melt-grown and possibly oxidized) Sn-based HaPs showed large RT mobilities of ~2000 cm^2/Vs.[7] A complete description of these two, perhaps separate, issues is currently lacking and we will not attempt to provide further explanations here. We summarize that identifying which scattering mechanisms determine the carrier transport, as observed in different mobility measurements, is an extremely intriguing and relevant open scientific question.

Soft lattice, anharmonicity and dynamic disorder One peculiar aspect of HaPs is that their lattice is rather soft mechanically, *i.e.*, elastic constants and phonon (vibrational) energies associated with the inorganic lattice are low. Again, this can be placed into a more general materials physics context, where the soft lattice of HaPs is neither surprising nor new, given that conventional soft materials can have elastic moduli orders of magnitude lower than HaPs. It can also be understood physically by considering that the relatively low formal ionic charges in the HaP structure result in a weak electrostatic interaction within the lattice. In the context of optoelectronic materials, though, this is somewhat special. While for silver iodide the modulus is comparable,[137] typical inorganic semiconductors that are used in efficient PV devices are much more rigid mechanically, with, *e.g.*, bulk moduli that are 3-10 times larger than those of HaPs (see Table 1).

The mechanical softness is interesting in itself as it has potential relevance for the (photo-)stability properties of HaP-based PV cells, and it triggers an additional observation. The Pb-halide optical vibrational modes are low in energy, and at RT they will be occupied by many quanta leading to very large halide displacements, as shown by the thermal ellipsoids extracted from neutron diffraction measurements shown in Figure 1b.[25] The displacements of the halides are so pronounced that *their motion can be expected to be* *sufficiently anharmonic to exhibit experimentally detectable signals of such anharmonicity*. At the same time, anharmonic and/or multi-well modes that correspond to the A-site cation,[138,139] such as molecular rotations of MA in hybrid- or Cs head-to-head motion in all-inorganic HaPs,[15] are also low in energy and, thus, strongly populated at RT. *The coexistence of several, highly anharmonic nuclear motions of different ions can be expected to lead to coupled anharmonic, multi-mode vibrational characteristics in HaPs at RT*.

Experimental evidence for these anharmonic, multi-mode fluctuations are the dynamic disorder of both the A-site cation[24] and the inorganic sublattice of HaPs at RT, as was shown with *T*-dependent Raman spectroscopy (see Ref. [15] and Figure 1c) and inelastic X-ray scattering.[26] It was also shown that a rotational disorder of the halides occurs due to light-induced, hot-electron scattering in time-resolved electron-scattering experiments.[140] *Importantly, as both Raman data and first-principles molecular dynamics calculations show,*[15] *these ionic displacements and their consequences cannot be described and understood completely in a conventional perturbative-like treatment within the harmonic approximation and a traditional phonon picture.* In particular, the nuclear motion that is associated with some of the halide and A-site cation modes is very slow, large in amplitude, and it is reflecting a multi-well behavior. Furthermore, some of the faster phonon modes in HaPs can change their frequency and mix into different phonons as these slow modes evolve. This indicates that the structural and dielectric fluctuations in HaPs show an intriguing time/frequency dependence, which poses an interesting multi-scale challenge to both experimental and theoretical techniques. Therefore, this behavior goes beyond "just" thermal fluctuations. Rather, it gives rise to coupled anharmonic polar fluctuations or, in other words, *dynamic disorder involving multiple polar vibrational modes*. We note that anharmonic effects are important for describing the phonon spectra of PbTe and SnTe,[141] and that this behavior is not one of Pb-halogen bonds *per se*, as was shown by comparing far-IR spectroscopy of PbI_2 and $MAPbI_3$, where at RT the latter shows much broader Pb-I peaks than the former, indicating anharmonic fluctuations in the Pb-I lattice of the latter.[132] While a "central peak" in Raman spectroscopy is associated with an incipient polar transition and known to occur for certain ferroelectric systems including oxide perovskites,[142,143] this is not known in materials of high optoelectronic quality at RT.

We note that the apparent contradiction between an ordered structure, as measured in a diffraction experiment (see Figure 1a), and the specific dynamic disorder, seen in Raman (see Figure 1c) and inelastic X-ray scattering measurements, can be explained within known physical models. Consider that XRD instantaneously probes a structural average over many unit cells and typically does not provide some of the frequency-dependent structural fluctuations that we have described above. Conversely, Raman intensities are determined by local fluctuations of the lattice that are coupled to the local electric field distribution and changes in the electronic polarizability. Thus, the static and dynamic structural information acquired is directly related to the applied spectroscopic technique, and conclusions about lattice order drawn from each type of measurement do not have to coincide *per se*. This tells us that a snapshot of the local HaP structure at RT may show strong deviations from the average one, including large-amplitude displacements of some of the ions.

Dynamic disorder and optoelectronic properties We emphasize again that what makes HaPs unique is the *combination* of properties a.-h. and i.-o., as listed in the introduction section and illustrated with selected data in Figure 1. In particular, the structural dynamics discussed in the previous section are uncommon for a material of high optoelectronic quality. These structural dynamics, *i.e.*, dynamic disorder in concert with anharmonic motions of several of the HaPs ions at RT, lead to a picture of HaPs where locally a strong structural distortion may appear, before it vanishes and appears again somewhere else in the crystal. Therefore, depending on the time- and length-scales of the interactions between probe and sample that determine the outcome of a certain experiment determining a device parameter, a structure that is significantly distorted and bent dynamically may be the relevant one rather than the average bulk crystal structure.

Following our description of the coupling between the anharmonic, multi-well nuclear motions in HaPs, we can attempt to provide relevant time- and length-scales of the structural fluctuations in HaPs. From the analysis of the Raman measurements in Ref. [15], the relaxation time of the structural fluctuations was found to be ~0.1 - 1 ns. Molecular dynamics calculations of $CsPbBr_3$ can be used to provide important information on the spatial extent of the coupling between modes,[15] *e.g.*, the outward motions of halide ions on a joint plane with A-site head-to-head motion that occurs in proximal unit cells, *i.e.*, coupling occurs on the order of a few Å. It is intriguing that HaPs show sharp optical absorption edges and low Urbach-energies at RT despite the anharmonic, large-amplitude nuclear motion of the halides, which determine the frontier occupied states in the band structure.

Open scientific questions and tentative answers Based on our discussion in this Essay, we can now address the following open scientific questions for the optoelectronic properties of HaPs:

1. *Why is the non-radiative recombination of HaPs so low, especially considering the way they can be synthesized?*
2. *Related to this, why is the density of optically and electrically active defects unusually low?*
3. *What are the relevant carrier-scattering phenomena that determine the carrier mobilities?*

In light of some of the unique structural dynamics of HaPs and other potentially important effects, we now consider what can already be said about these remaining issues.

Low non-radiative recombination rate To explain the low rates and long carrier lifetimes of HaPs, different hypotheses were put forward in the literature, including

(i) the influence of the Rashba effect and indirect band gap,[49,144–146,146,147]
(ii) the low density of deep intrinsic defects, due to their high formation energies,[66] and
(iii) the existence of unusual polaronic effects.[148,149]

The fact that recombination in HaPs is much slower than predicted by equations for diffusion-limited recombination (such as the Langevin equation) indicates that recombination is limited by the time needed to dissipate the energy of the electron-hole pair (as in inorganic semiconductors, *e.g.*, GaAs and GaP[150]). This energy dissipation *via* the emission of phonons becomes more unlikely, the higher the number of phonons is that have to be dissipated at the same time. Therefore, a clear description of defect properties is essential to understand non-radiative recombination in inorganic but less so in organic semiconductors.[151] In organic semiconductors, the high energy of internal vibrational modes (~160 meV)[151] reduces the number of phonons that have to be excited simultaneously for non-radiative recombination to happen. As emphasized above, HaPs have very low phonon energies due to the high reduced mass of the atomic oscillator (~16 meV for the Pb-I related LO phonon of $MAPbI_3$).[132] Therefore, in analogy to the disadvantage of organic solar cells in terms of high open-circuit voltage losses due to non-radiative recombination, the long lifetimes of HaPs may be explained by the low optical phonon energies in these systems.[152]

One currently open question related to non-radiative recombination is that there is evidence for non-radiative band-to-band recombination[153,154] contributing to the total bimolecular recombination coefficient. This non-radiative term cannot originate from multiphonon transitions as discussed above and therefore must have another origin. One suggestion in the literature is that Auger recombination, involving at least one trapped charge carrier, is responsible for these results.[153] While this is a possible mechanism, further work is needed to clarify this point.

In this context, it is important to note that HaPs can exhibit a Rashba effect: owing to the large spin-orbit coupling (SOC) in HaPs and possible polar distortions, the spin-degeneracy of the conduction and valence bands are lifted, which can also lead to an indirect band-gap.[49,144–146,146,147] When the spin-textures of the conduction and valence band are opposite, the radiative recombination of photoexcited electrons and holes is slowed down substantially, as it is a spin-forbidden transition that would require a spin flip.[49] How the Rashba effect and indirect band-gap impact non-radiative lifetimes is currently an open question.[147]

Why is the density of optically and electrically active defects so low? Generally, both the experimental and theoretical literature related to defect levels in HaPs are vastly scattered,[66,155–158] making it difficult to draw generally valid conclusions. However, that defects in HaPs are benign in an optoelectronic sense must hold true nevertheless, given the outstanding device properties for a material made by using low-energy and -temperature fabrication. In view of our perspective that HaPs show structural fluctuations at certain time- and length-scales, we wonder how this may affect defect trap densities and levels in different optical and electrical measurements, which naturally probe the system on different time-scales. It is interesting in this context that a polycrystalline HaP thin film can show an open-circuit voltage that is barely 100 mV below the highest theoretically possible one at RT without light concentration. This result implies that defect states, both inside grains and those due to grain boundaries, must be mostly benign as found in "early" experiments [36,37] – again, from an optoelectronic viewpoint. Moreover, distinct experimental techniques that probe defect energetics and kinetics differently lead to different conclusions.[156–160] It may well be the case that the dynamic structural and electronic distortions in HaPs appear or do not appear as an optical or electrical defect in a given experiment.

Charge-carrier scattering and mobilities In a similar spirit, when charge carriers migrate through HaPs, their scattering appears on similar time scales as the dynamic structural fluctuations discussed above. Indeed, given the anharmonic, large amplitude nature of these structural fluctuations, this may explain why typical scattering models cannot fully explain results from mobility experiments. Also, it needs to be emphasized that the experimentally observed values for the mobility do depend somewhat on the technique used, *e.g.*, for $MAPbI_3$ results extracted from a time of flight and space-charge limited current measurement vary by a factor of seven.[124]

Theoretical models clearly need to take the dynamic fluctuations of HaPs fully into account. As has been shown recently by some of us,[161] a model that takes into account the effect of large-amplitude anharmonic structural fluctuations on the electronic properties can explain the modest mobility of $MAPbI_3$ at RT as well its T-dependence. Interestingly, some important effects considered in this model, especially the off-diagonal scattering of electrons and holes, are typically deemed unimportant for inorganic semiconductors. But our recent results have shown that these are essential to the understanding of carrier transport in HaPs. Furthermore, recent results and analysis on the emission Stokes shift in HaPs point to similar conclusions:[162] while the optical phonon energy of $CsPbBr_3$ is similar to that of CdTe, and thus the phonon occupation at RT is essentially the same, the T-dependence of the Stokes shift in hybrid and all-inorganic HaPs cannot be explained within a purely harmonic phonon model, in contrast to what is the case for CdTe.

Finally, another open question that we would like to point out concerns the electron versus hole mobility of HaPs. Several experimental studies have shown that holes are more mobile than electrons, see, *e.g.*, Refs. [124,163]. Given that the electron and hole effective masses are rather similar (see Table 1), we are not aware of a full microscopic description of this observation.

Summary As emphasized throughout this Essay, HaPs display a combination of material properties that, while not unprecedented separately, are unique within one material. As highlighted in the previous sections, it is our contention that in particular the anharmonic, multi-mode lattice fluctuations in a material that is an otherwise excellent semiconductor lie at the heart of making HaPs so special. In contrast to typical inorganic PV materials, a separation of different effects, acting either on the electronic structure or on ionic movements, is more complicated in HaPs. Intriguing structural dynamics, transcending the harmonic phonon picture, can be coupled to the electronic structure, optical excitations, and electrical effects at different time- and length-scales. The open scientific questions that are most deserving in this context have been highlighted here. All of these questions are also likely to be relevant for technological device applications. We conclude that basic notions of semiconductor physics, including concepts such as phonons, polarons, defects, etc., and how these are related to different optoelectronic observables, have to be applied and used with care for HaPs. Our aim here is not to question these fundamental models and their validity for HaPs as such. Rather, it is to point out that these models use assumptions that, while normally well-grounded, may not hold true given the unusual structural fluctuations in HaPs at RT. Following the major issues discussed in this article, we postulate that in order to make progress in understanding these materials *per se,* and to extract from them guidelines in the search of other materials of this type as well as to help improve the materials for devices made from them, going beyond these concepts is likely necessary.

Acknowledgments DAE acknowledges funding provided by the Alexander von Humboldt Foundation within the framework of the Sofja Kovalevskaja Award endowed by the German Federal Ministry of Education and Research. At the WIS this work was supported in part by its Sustainability And Energy Research Initiative (SAERI). TK acknowledges support from the DFG (Grant Nos. KI-1571/2-1), RL by the German Federal Ministry of Education and Research (FKZ 13N13656), and AMR by the US Office of Naval Research, under grant N00014-17-1-2574.

Note added in print An example for the dynamic character of the field is that on the day of acceptance of this article, a study on time-of-flight ("Haynes-Shockley") measurements of (drift) mobility was published.[164] In that article, a T-dependence of μ in $MAPbI_3$ single crystals is reported with an exponent, around RT, of -2.8 and -2.0 for electrons and holes, respectively. If reproduced, this result will need to be reconciled with the roughly $\mu \sim T^{-1.5}$ dependence, derived from photo-Hall, microwave conductivity and time-resolved THz experimental results on this and other HaPs.

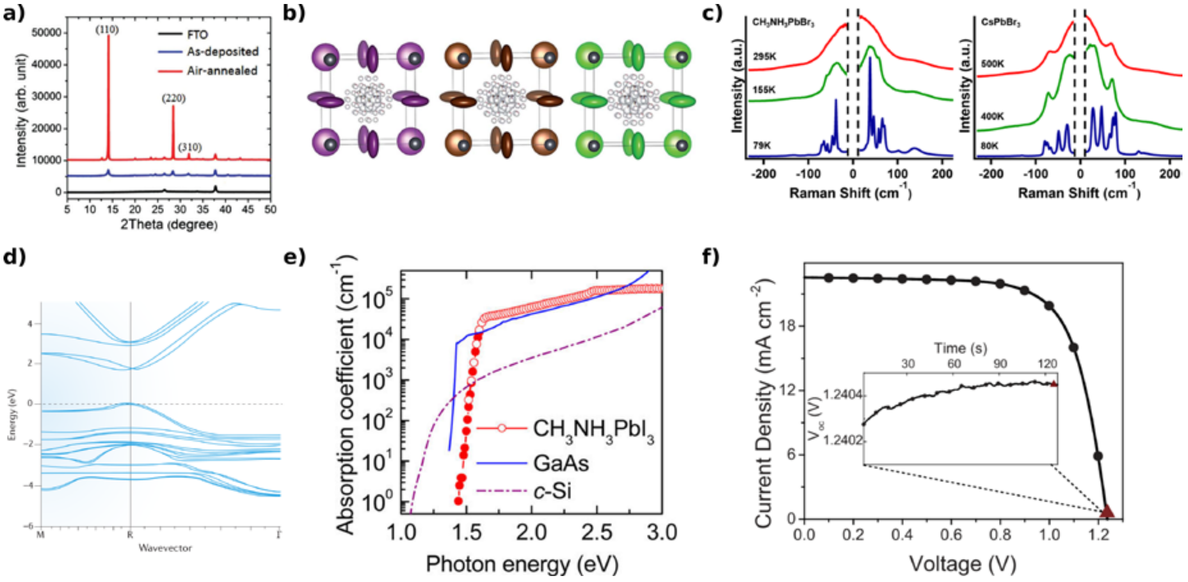


Figure 1: Halide perovskites (HaPs) exhibit a *unique combination of structural and optoelectronic properties*: the *upper part* (a-c) shows selected data associated with the former and the *lower part* (d-f) the same for the latter. a) X-ray diffraction (XRD) spectra of as-deposited and air-annealed $MAPbI_3$ films (annealing was performed at 150 °C for 15 min). b) Refined structures of $MAPbX_3$ single crystals (with X being I, Br, and Cl, from left to right) obtained from XRD and neutron diffraction experiments showing the disordered arrangement of the MA groups and large displacement ellipsoids of the halides. c) Low-frequency Raman spectra of hybrid and inorganic HaPs in the orthorhombic (blue), tetragonal (green), and cubic phase (red), showing growth of the central peak with temperature in both materials. d) Electronic band structure of cubic-phase $MAPbI_3$ calculated with many-body perturbation theory in the GW approximation. M, R and Γ correspond to (1/2, 1/2, 0), (1/2, 1/2, 1/2) and (0, 0, 0) k-points, respectively. e) Effective absorption coefficient of a $MAPbI_3$ thin film compared with GaAs and crystalline silicon (c-Si), all measured at room temperature. f) Current-voltage curve of high open-circuit voltage (V_{oc}) device made with a (Rb,Cs,MA,FA) HaP alloy as the absorber material (optical gap: 1.63 eV). The inset shows the V_{oc} as function of time resulting in 1240 mV, which is displayed as the red triangles in both plots. Panel a) reproduced from Ref. [9] with permission, copyright 2015, Wiley. Panel b) reproduced from Ref. [25] with permission from The Royal Society of Chemistry. Panel c) reprinted with permission from Ref. [15], copyright 2017 by the American Physical Society. Panel d) reproduced from Ref. [5] based on data originally reported in Ref. [28] with permission, Nature publishing group. Panel e) reproduced from Ref. [31] with permission, American Chemical Society. Panel f) reproduced from Ref. [61] with permission, American Association for the Advancement of Science.

Table 1: Electron and hole effective masses and mobilities[*], as well as bulk moduli, for different semiconductors used in high-quality PV devices.

material	h^+ effective mass (m_e)	e^- effective mass (m_e)	μ_{h+} (cm^2/Vs)	μ_{e-} (cm^2/Vs)	T-dependence of μ_{h+}, μ_{e-}	bulk modulus (GPa)
Si[+]	0.54 [109]	0.32 [110]	500 [109]	1500 [110]	$T^{-2.2}$, $T^{-2.4}$ [111]	98 [112]
GaAs[+]	0.53 [113]	0.06 [113]	400 [113]	8000 [113]	$T^{-2.3}$, $T^{-2.3}$ [113]	75 [114]
CdTe[+]	0.72 [115,116]	0.11 [115,116]	100 [117]	1100 [117]	$T^{-1.8}$, T^{-2} [115,116,118]	42 [119]
$CuInS_2$	~1[120]	0.16 [120]	~20 [120]	~150 [120]	$T^{-2.1}$, $T^{+1.5}$ [120]	75 [121]
$MAPbI_3$	0.26 [122,123]	0.23 [122,123]	≤160 [124]	≤70 [124]	$T^{-1.5}$ [42,125]	5 [126]
$MAPbBr_3$[§]	0.15 [127]	0.25 [127]	≤220 [128]	≤190 [129]	$T^{-1.4}$ [43]	20 [14]

[*] The *T*-dependences of the mobilities that are given are those around RT.

[+] The density-of-state effective masses for holes were calculated from the light and heavy hole masses, which are dominated by the heavy hole mass.

[§] The electron mobility derived from using terahertz time-domain spectroscopy is 80 cm^2/Vs and the hole mobility is 270 cm^2/Vs.

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