Research Update: Relativistic origin of slow electron-hole recombination in hybrid halide perovskite solar cells

Pooya Azarhoosh, Scott McKechnie, Jarvist M. Frost, Aron Walsh, and Mark van Schilfgaarde

Citation: APL Mater. 4, 091501 (2016); doi: 10.1063/1.4955028
View online: http://dx.doi.org/10.1063/1.4955028
View Table of Contents: http://scitation.aip.org/content/aip/journal/aplmater/4/9?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
An experimentally supported model for the origin of charge transport barrier in Zn(O,S)/CIGSSe solar cells
Appl. Phys. Lett. 108, 043505 (2016); 10.1063/1.4940913

Impact of carrier recombination on fill factor for large area heterojunction crystalline silicon solar cell with 25.1% efficiency
Appl. Phys. Lett. 107, 233506 (2015); 10.1063/1.4937224

Mechanism of charge recombination in meso-structured organic-inorganic hybrid perovskite solar cells: A macroscopic perspective
J. Appl. Phys. 117, 155504 (2015); 10.1063/1.4918722

Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells
J. Appl. Phys. 97, 114302 (2005); 10.1063/1.1901835

Temperature dependent electron beam induced current experiments on chalcopyrite thin film solar cells
Appl. Phys. Lett. 70, 1011 (1997); 10.1063/1.118467
Research Update: Relativistic origin of slow electron-hole recombination in hybrid halide perovskite solar cells

Pooya Azarhoosh,1 Scott McKechnie,1 Jarvist M. Frost,2 Aron Walsh,2,3 and Mark van Schilfgaarde1,a

1Department of Physics, Kings College London, London WC2R 2LS, United Kingdom
2Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
3Global E3 Institute and Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, South Korea

(Received 11 April 2016; accepted 14 June 2016; published online 21 July 2016)

The hybrid perovskite CH₃NH₃PbI₃ (MAPI) exhibits long minority-carrier lifetimes and diffusion lengths. We show that slow recombination originates from a spin-split indirect-gap. Large internal electric fields act on spin-orbit-coupled band extrema, shifting band-edges to inequivalent wavevectors, making the fundamental gap indirect. From a description of photoluminescence within the quasiparticle self-consistent GW approximation for MAPI, CdTe, and GaAs, we predict carrier lifetime as a function of light intensity and temperature. At operating conditions we find radiative recombination in MAPI is reduced by a factor of more than 350 compared to direct gap behavior. The indirect gap is retained with dynamic disorder.

Metal-organic perovskite solar cells, CH₃NH₃PbI₃ (MAPI) in particular, have attracted much recent attention because of their high power conversion efficiency and potential low cost. The material exhibits strong absorptivity characteristic of a direct-gap semiconductor, with the slow radiative recombination characteristic of an indirect-gap semiconductor. The minority carrier diffusion length considerably exceeds the material thickness required for complete solar capture. As such, internal quantum efficiencies approach 100%. Power conversion efficiencies as high as 21% have been reported. The constituent elements are abundant and efficient devices can be made with solution processing methods which offer the potential for low-cost and large scale production. MAPI is thus perhaps the first competitive realization of a “third generation” solar cell.

Minority carrier recombination lifetimes of tens of microseconds are reported in MAPI by time-resolved photoluminescent (TRPL) spectroscopy and other methods. Such long lifetimes are found in high-quality samples of crystalline silicon, the archetype indirect-gap semiconductor. A variety of trap-based models have been used to interpret the TRPL data. These models suggest that the long lifetimes are due to immobilization of charges in traps. However, samples (both single- and poly-crystalline) with trap density differences of the order 10⁵ have lifetime variations of only an order of magnitude. This suggests that lifetime is weakly correlated with measured trap density. Further, longer lifetimes are observed in low trap-density single-crystal samples.

We show that the observed slow radiative recombination is an intrinsic property of MAPI due to the details of the electronic band structure. We formulate the recombination rate in the framework of the quasiparticle self-consistent GW (QSGW) approximation. A spin-split indirect-gap is formed. Assuming charge carriers thermalize rapidly within a band, we calculate recombination as a function of charge density (illumination intensity) and temperature. With low doping density and solar illumination intensities, the material exhibits an indirect-gap. We show that under operating solar

---

aElectronic mail: mark.van_schilfgaarde@kcl.ac.uk
FIG. 1. Electronic band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$. (a) schematic of absorption and recombination processes. The conduction bands (red) are split around $R$, as opposed to conventional direct-gap semiconductors, where there is a single minimum. Photon absorption (dark grey arrows) generate electron-hole pairs, which quickly thermalize to their respective band edges (dark gray arrows) creating a quasi-equilibrium distribution of carriers (red and green). The excess electrons and hole populations can recombine, creating a photon in the process (light grey arrow). Without phonon assist the transitions must be vertical, as shown. If the electron and hole populations are small, the volume of overlapping $k$ space between the red and green distributions becomes exponentially small in $1/k_B T$, while in CdTe and GaAs the two populations occupy the same phase space for any concentration. (b) QS$GW$ band structure for a section of the $M$–$R$–$\Gamma$ lines. There is a significant splitting of the conduction band near $R$ ($E \sim 1.75$ eV), and a much smaller splitting of the valence band, near ($E = 0$).

In cell conditions, radiative recombination rate is suppressed by over 350 fold; moreover, it varies in an anomalous manner, increasing rapidly with temperature, and illumination intensity and doping. This is in contra-distinction to semiconductors such as CdTe or GaAs, whose recombination properties are also calculated.

For crystals without inversion symmetry, spin-orbit coupling (SOC) splits spin-degenerate levels in non-magnetic systems. In MAPI, significant local electric fields, acting on the large SOC contribution from the heavy lead atom, generate a significant shift in the spin-degenerate conduction band minimum of Pb 6$p$ character. This minimum splits into a pair of minima antipodal to the original point, causing the gap to become slightly indirect (Fig. 1). We investigate the effect of dynamic disorder on this spin splitting. Our initial model is a single unit cell, with an infinite array of aligned organic moieties. In reality, the organic moiety rotates on a picosecond time scale at room temperature. We sample molecular dynamics realizations of a disordered supercell. In spite of the disorder, the spin-split indirect-gap is not only present but enhanced.

The band splitting is a robust property of the material in working solar cells that suppresses radiative recombination of minority charge carriers, enhancing the photovoltaic action. Two recent studies have noted the importance of the formation of an indirect band gap on the recombination rate of MAPI. In Ref. 13, an indirect gap was observed for certain molecular orientations. In Ref. 14, the indirect band gap is recognized as the result of Rashba splitting, leading to a mismatch in both momentum and spin. While their work emphasizes spin mismatch, we believe that the momentum-mismatch dominates device performance as the valence bands are only slightly split, and geminate recombination is likely to be a minor process.

In this letter, we report the recombination rate with spin-orbit coupling included in the Hamiltonian, thus directly treating both spin and momentum mismatch. To our knowledge, the only comparable calculation of radiative recombination was by Filippetti et al. where the rate was calculated from density-functional theory without the spin-orbit coupling that is essential for both momentum and spin mismatch.

Above 162 K, MAPI undergoes a continuous transition from a tetragonal to a pseudocubic structure. At room temperature the tetragonal distortion is small, $c/2a \approx 1.01$. The organic moiety in MAPI has a relatively low barrier to rotation and rotates at room temperature in a quasi-random fashion. On average the structure can be considered to be cubic. We initially construct a model with a single formula unit of $\text{CH}_3\text{NH}_3\text{PbI}_3$. We orient the organic moiety along [100], [110], and

reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 155.198.8.192 On: Fri, 07 Oct 2016 15:04:02
[111], where local potential energy minima are found, which generate three structures representative of the disordered system.

In the absence of spin-orbit coupling the valence band maximum (VBM) and conduction band minimum (CBM) \( k_{\text{min}} \) lie at the \( \langle 111 \rangle \) \( R \) point.\(^5\)\(^6\) The former consists mainly of I \( 5p \) character, the latter mainly Pb \( 6p \). The degeneracy of both extrema is split and displaced by spin-orbit coupling \((\langle \xi(r) \rangle \mathbf{L} \cdot \mathbf{S})\), which originates near the atomic cores where \( \xi(r) \) is large (Fig. 1). \( \langle \xi \rangle \) scales approximately as \( Z^2 \).

With Pb being so heavy (\( Z = 82 \)), \( \langle \xi \rangle \mathbf{L} \cdot \mathbf{S} \) strongly affects the lead \( 6p \) conduction band, spin-splitting the minima into a pair of distinct states offset from \( R \) (Fig. 1). The iodine \( 5p \) valence band is affected to a lesser extent (\( Z = 53 \)), the spin-split displacement is small, resulting in a flattened region in reciprocal space due to the overlapping minima. The spin-orbit coupling narrows the band gap by \( \sim 1 \) eV. The spin splitting is linear in \( k \), in contrast to typical semiconductors where it varies as \( k^3 \). The band gap thus becomes slightly indirect. The direct band gap \( E_0 \) remains at \( R \) and is 75 meV larger than the indirect gap.

The joint density-of-states (JDOS), relevant for absorption, differs from its direct-gap values in only a small energy range around \( E_0 \). The flattened valence band contributes to a large density of states available for optical transition at the direct-gap. Thus absorption is only slightly affected by the spin-splitting: MAI absorbs solar radiation as though it were a direct-gap semiconductor. However, radiative recombination is dramatically suppressed. This is extremely unusual for a solar cell material, where typically emission and absorption are the direct reverse of one another. Photoexcited electrons (holes) rapidly thermalize to a small region of \( k \) space centered at the conduction (valence) band edges. The asymmetry in \( k_{\text{CBM}} \) and \( k_{\text{VBM}} \) means that there is a low joint density-of-states of the thermalized minority carriers. Direct \((k\text{ conserving})\) recombination is thereby reduced.

Higher temperature leads to greater thermal broadening and a larger overlap in the joint density-of-states, increasing radiative recombination. High density of photogenerated charges (or extrinsic charge carrier doping) fills the small pockets at the CBM. Radiative recombination increases critically, reverting to direct-gap semiconductor behaviour. This property is intrinsic to the material; no defect or trap states are needed to explain why radiative recombination is suppressed at low photon flux but increase dramatically at high photon flux. There is some evidence for such behaviour: carrier lifetimes demonstrate a sharp fall at moderate injection densities.\(^7\)

Here we formulate an \textit{ab initio} theory for radiative recombination within the QS\( \text{SGW} \) approximation.\(^17\) QS\( \text{SGW} \) is parameter free. In \( sp \) semiconductors a wide range of electronic properties are uniformly well described,\(^18\) including splitting from the Dresselhaus terms.\(^19\) Few fully \textit{ab initio} formulations of radiative recombination have been reported.\(^20\) Calculations using the van Roosbroeck-Shockley relation with experimental\(^21\) and theoretical\(^22\) absorption coefficients have been published. We directly calculate the recombination rate without model parameters, adapting the standard theory of dielectric response to non-equilibrium carrier populations.

The recombination dynamics of carriers within the bulk of an intrinsic semiconductor \((n = p)\) can often be accurately described by a third-order rate equation

\[
\frac{dn}{dt} = G - nA - n^2B - n^3C. \tag{1}
\]

Here \( n \) is the density of excited carriers and \( G \) is a source term describing constant photogeneration of carriers.\(^23\) These parameters are often fit to experimental transient data across a large range of laser fluences and thus carrier densities.\(^24\) An implicit assumption is that these coefficients do not vary across the carrier density regime experimentally accessed. \( A \) is related to the one-body non-radiative carrier recombination, which proceeds through crystal defect levels as intermediate states. We are concerned with intrinsic recombination and do not consider this extrinsic process. \( C \) is the three-body Auger recombination coefficient. This has been calculated in a \( GW \) framework\(^25\) but it becomes important under strongly non-equilibrium carrier populations and we omit it here. The two-body coefficient \( B \) describes radiative recombination of free carriers and is intimately connected with both absorption and emission. Photo-generated carriers thermalize to the band edges on a picosecond time scale,\(^26\) which is fast compared to the radiative recombination time (ns to \( \mu \)s).
We will assume that photoexcited carriers thermalize instantaneously within a band to form quasi-equilibrium Fermi-Dirac distributions of electrons and holes. Thus the occupation probability of an excited electron \( c \) is given by

\[
f_c = \left( \exp\left[\frac{(E_c - E^F_{c})}{k_B T}\right] - 1 \right)^{-1},
\]

where \( E_c - E^F_{c} \) is the excitation energy relative to the electron quasi-Fermi level. The corresponding distribution \( f_n \) for excited holes is the same form, substituting \( E_c - E^F_{c} \) \( \rightarrow \) \( E_v - E^F_{v} \). In practice, we specify \( T \), and electron and hole populations \( n \) and \( p \). From the QSGW band structure we can calculate the density of states and so determine \( E^F_{c} \) and \( E^F_{v} \) from \( n \) and \( p \).

To establish that QSGW can reliably predict the photoluminescent process, we compute \( B \) for the benchmark materials GaAs and CdTe. This both validates the method developed here and serves as points of comparison to MAPI.

Under solar intensities a small population of electrons (holes) is excited to the conduction (valence) band (Fig. 1). This density is relatively small for an operating solar cell (as points of comparison to MAPI).  

Numerically, this necessitates a fine \( k \) mesh to adequately sample the near regions of the band minima. Some additional modest approximations are necessary to make the calculation tractable. We neglect local fields and use the independent-particle (time-dependent Hartree) approximation. This approximation misses the Wannier excitons below the band edge, but they are very shallow.\(^{27,28}\) If the potential is local,

\[
\epsilon(\omega) = \sum_{k \in \text{cv}} \epsilon_{k \text{cv}}(\omega)
\]

\[
\text{Im} \epsilon_{k \text{cv}}(\omega) = \frac{1}{\hbar} \frac{2\pi e^2}{m \omega} |P_{k \text{cv}}|^2 f_{c}(1 - f_{v}) \delta(\omega - \omega_{k \text{cv}}).
\]

\( \epsilon_{k \text{cv}} \) resolves \( \epsilon \) into individual electron-hole excitations between Bloch states \( v \) and \( c \); \( \hbar \omega_{k \text{cv}} = E_v(k) - E_c(k) \) is the excitation energy of the \( \text{cv} \) pair. The photons couple \( c \) to \( v \), which for direct transitions simplifies to a matrix element of the momentum operator \( P_{k \text{cv}} \). We omit phonon-assisted indirect transitions that do not conserve \( k \) because they are weaker, higher-order processes. As written Eq. (3) is approximate because the QSGW potential is non-local. However, for transitions close to \( E_0 \) the effect of non-locality can be described by a scaling of \( P_{k \text{cv}} \).\(^{29}\) Further details of the theory are given in the supplementary material.\(^{30}\)

By resolving \( \text{Im} \epsilon \) into individual pair contributions, the transition rate (Einstein coefficient) \( A_{k \text{cv}} \) between a \( \text{cv} \) pair can be readily identified,

\[
A_{k \text{cv}} = \frac{n_e e^2 \omega_{k \text{cv}} |P_{k \text{cv}}|^2}{\pi \epsilon_0 \hbar c^3 m^2},
\]

and the energy-resolved radiative recombination rate is

\[
R_{k \text{cv}}(\omega) = f_{c}(1 - f_{v})A_{k \text{cv}} \delta(\omega - \omega_{k \text{cv}}).
\]

The total emission rate

\[
R^{\text{tot}} = \int_0^\infty d\omega \sum_{k \text{cv}} R_{k \text{cv}}(\omega)
\]

is conventionally expressed in terms of a carrier density independent recombination lifetime \( \tau \) or a B coefficient

\[
\tau^{-1} = B n = R^{\text{tot}} / n.
\]
FIG. 2. Radiative recombination coefficient for varying temperature and excitation intensity. (a) Radiative recombination coefficient $B$ in the intrinsic case $n = p$. $B$ for CdTe, GaAs, and MAPI at room temperature, varying photoexcitation density $n$. All have comparable direct band gaps and effective masses. At $n > 10^{18}{\text{cm}}^{-3}$ the MAPI spin-split indirect-gap saturates and the rate of radiative recombination becomes similar in all three materials. Also shown are MAPI calculated at 200 K and 400 K. The effect of the indirect gap becomes more pronounced as $T$ decreases. (b) Temperature dependence of radiative recombination for $n = 10^{16}{\text{cm}}^{-3}$.

The magnitude of $B$ increases as the $k$-space overlap between electron and hole distributions increases. This causes the rate of bimolecular recombination to depend on external parameters in an unusual manner. For example, increasing temperature smears $f_c$ and $f_v$ over a wider band of $k$ for fixed $n$, causing $B$ to increase with $T$. The temperature dependence of $B$ in GaAs and CdTe (Fig. 2) is weaker and of opposite sign. Further, bimolecular recombination will increase abruptly with photoexcited carrier density once the electron pockets begin to fill up and overlap ($n \sim 10^{18}{\text{cm}}^{-3}$ in Fig. 2), in sharp contrast to CdTe and GaAs. Only at high carrier concentrations when a significant fraction of electrons and holes overlap does $B$ in MAPI become comparable to $B$ in CdTe, where it also adopts the conventional behaviour and begins to decrease with increasing $n$. The strong carrier density, and therefore laser-fluence, dependence of $B$ suggests that global fits to time resolved data are not a reliable method to infer $B$ or lifetime from $B$ (Equation (7)). The variation of $B$ with carrier density will make high fluence transients multi-exponential and break the expected relationship between light-emission and carrier-density sensitive experimental probes.

For photoexcitation densities $n < 10^{17}{\text{cm}}^{-3}$ ($n = p$), we find $B \approx 4 \times 10^{-13}$ at room temperature. These are the charge carrier densities relevant for device operation in sunlight. As $B$ is fairly constant below this charge carrier density, we can use Equation (7) to derive a lifetime of order $\tau$.

| Material | $B$ (cm$^{-3}$s$^{-1}$) | $\tau$ (ns) |
|----------|-------------------------|--------------|
| MAPI     | See text                | 0.49         |
| GaAs     | 35–37                   | 267          |
| CdTe     | 38–40                   | 195          |
| Si       | 41,42                   | 0.001–0.01   |
Calculated values of $k_{\text{min}}$ and conduction band effective masses along the three principal axes. LDA results for the molecular dynamics $2 \times 2 \times 2$ supercell are the average from one hundred snapshots.

| Structure          | Theory       | $k_{\text{min}}$ (Å$^{-1}$) | $m_1$ | $m_2$ | $m_3$ |
|--------------------|--------------|----------------------------|-------|-------|-------|
| Pseudocubic (100)  | QSGW         | 0.043                      | 0.95  | 0.13  | 0.11  |
| Pseudocubic (110)  | QSGW         | 0.055                      | 0.13  | 0.11  | 0.11  |
| Pseudocubic (111)  | QSGW         | 0.043                      | 0.36  | 0.12  | 0.12  |
| Pseudocubic (100)  | LDA          | 0.049                      | 1.03  | 0.09  | 0.06  |
| Pseudocubic (110)  | LDA          | 0.057                      | 0.08  | 0.07  | 0.06  |
| Pseudocubic (111)  | LDA          | 0.049                      | 0.27  | 0.08  | 0.08  |
| Molecular Dynamics |              | 0.105                      | 1.02  | 0.60  | 0.42  |
limited body of evidence to support the latter; along these lines it is noteworthy that high power
conversion efficiencies have been reported only for lead-based halide perovskites. This is consistent
with the spin-split indirect gap picture, as SOC is weaker in lighter elements such as Sn. In principle
it is possible to obtain experimental evidence for the direct/indirect-gap picture, with optical probes
of the (weakly emissive) indirect gap. Sensitive photoluminescence (PL) or electroluminescence
(EL) would probe the emission from this state, absorption can be probed by sensitive external
quantum efficiency (EQE) or photo-deflection spectroscopy (PDS). In our idealized structure we
predict the splitting to be 75 meV, while in the actual, disordered case it will vary with the disorder.

In summary we have provided a fully \textit{ab initio} relativistic calculation of the hybrid halide
perovskite radiative recombinative lifetime. We considered only direct recombination, and with
electron and hole populations described by a quasi-Fermi level. We have shown that the bimolecular
recombination rate is strongly temperature and carrier density sensitive and that the long carrier
lifetime and diffusion length are a direct consequence of large relativistic spin-orbit coupling
combined with internal electric fields. We suggest that the relevant electric fields are mainly generated
by dynamic deformation of the inorganic octahedral cage. The spin-split indirect gap is generated
by the Pb lone-pair driven distortions and the Pb spin-orbit coupling of the conduction band.
For perovskite alloys, for example, formamidinium/methylammonium/caesium and iodine/bromine,
the additional symmetry breaking due to occupational site disorder would be expected to further
enhance these effects, which is consistent with their strong photovoltaic action.

The authors thank Jenny Nelson, Thomas Kirchhart, and Keith Butler for useful discussions.
The research has been supported by the EPSRC (Grant Nos. EP/K016288/1, EP/M009580/1, and
EP/M009602/1), the Royal Society, and the European Research Council (No. 277757). Computational
tools were provided by the University of Bath and the EPSRC (Grant No. EP/L000202).

1 Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn, and P. Meredith, \textit{Nat. Photonics} \textbf{9}, 106 (2015).
2 H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang, \textit{Science} \textbf{345}, 542 (2014).
3 M. Green, \textit{Solar Cells: Operating Principles, Technology, and System Applications}, Prentice-Hall Series in Solid State
Electronics (Prentice-Hall, 1982).
4 Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, and J. Huang, \textit{Science} \textbf{347}, 967 (2015).
5 D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y.
Losovsky, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, and O. M. Bakr, \textit{Science} \textbf{347}, 519 (2015).
6 S. D. Stranks, V. M. Burlakov, T. Leijtens, J. M. Ball, A. Goriely, and H. J. Snaith, \textit{Phys. Rev. Appl.} \textbf{2}, 034007 (2014).
7 Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya, and Y. Kanemitsu, \textit{J. Am. Chem. Soc.} \textbf{136}, 11610 (2014).
8 F. Brivio, K. T. Butler, A. Walsh, and M. van Schilfgaarde, \textit{Phys. Rev. B} \textbf{89}, 155204 (2014).
9 E. Mosconi, C. Quarti, T. Ivanovska, G. Ruani, and F. De Angelis, \textit{Phys. Chem. Chem. Phys.} \textbf{16}, 16137 (2014).
10 M. T. Weller, O. J. Weber, P. F. Henry, A. M. Di Pippo, and T. C. Hansen, \textit{Chem. Commun.} \textbf{51}, 4180 (2015).
11 A. M. A. Leguy, J. M. Frost, A. P. McMahon, V. G. Sakai, W. Koelkelmann, C. Law, X. Li, F. Foglia, A. Walsh, B. C. O’Regan,
J. Nelson, J. T. Cabral, and P. R. F. Barnes, \textit{Nat. Commun.} \textbf{6}, 7124 (2015).
12 A. A. Bakulin, O. Selig, H. J. Bakker, Y. L. Rezus, C. Miller, T. Glaser, R. Lovrincic, Z. Sun, Z. Chen, A. Walsh, J. M. Frost,
and T. L. C. Jansen, \textit{J. Phys. Chem. Lett.} \textbf{6}, 3663 (2015).
13 C. Motta, F. El-Mellouhi, S. Kais, N. Tabet, F. Alharbi, and S. Sanvito, \textit{Nat. Commun.} \textbf{6}, 7026 (2015).
14 F. Zheng, L. Z. Tan, S. Liu, and A. M. Rappe, \textit{Nano Lett.} \textbf{15}, 7794 (2015).
15 J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, and A. Walsh, \textit{Nano Lett.} \textbf{14}, 2584 (2014).
16 M. Kim, J. Im, A. J. Freeman, J. Ihm, and H. Jin, \textit{Proc. Nat. Am. Soc.} \textbf{111}, 6900 (2014).
17 Our implementation was adapted from the original ecal code at https://github.com/tkotani/ecalj and available at http://www.
lnsuite.org/.
18 M. van Schilfgaarde, T. Kotani, and S. Faleev, \textit{Phys. Rev. Lett.} \textbf{96}, 226402 (2006).
19 A. N. Chantis, M. van Schilfgaarde, and T. Kotani, \textit{Phys. Rev. Lett.} \textbf{96}, 086405 (2006).
20 G. Lasher and F. Stern, \textit{Phys. Rev.} \textbf{133}, A553 (1964).
21 C. Barugkin, J. Cong, T. Duong, S. Rahman, H. T. Nguyen, D. Macdonald, T. P. White, and K. R. Catchpole, \textit{J. Phys. Chem.
Lett.} \textbf{6}, 767 (2015).
22 A. Filipetti, P. Delugas, and A. Mattoni, \textit{J. Phys. Chem. C} \textbf{118}, 24843 (2014).
23 E. Kiontakis, Q. Yan, D. Steifauf, and C. G. V. de Walle, \textit{New J. Phys.} \textbf{15}, 125006 (2013).
24 L. Milot, G. E. Peryton, H. J. Snaith, M. B. Johnston, and M. L. Her, \textit{Adv. Funct. Mater.} \textbf{25}, 6218 (2015).
25 T. Kotani and M. van Schilfgaarde, \textit{Phys. Rev. B} \textbf{81}, 125201 (2010).
26 M. B. Price, J. Butkus, T. C. Jellicoe, A. Sadhanala, A. Brian, J. E. Halpert, K. Broch, J. M. Hodgkiss, R. H. Friend, and
F. Deschler, \textit{Nat. Commun.} \textbf{6}, 8420 (2015).
27 J. Even, L. Pedesseau, and C. Katan, \textit{J. Phys. Chem. C} \textbf{118}, 11566 (2014).
28 A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, and R. J. Nicholas, \textit{Nat. Phys.
11}, 582 (2015).
29 R. Del Sole and R. Girlanda, \textit{Phys. Rev. B} \textbf{48}, 11789 (1993).
See supplementary material at http://dx.doi.org/10.1063/1.4955028 for further technical details of the recombination rate model.

T. Etienne, E. Mosconi, and F. D. Angelis, J. Phys. Chem. Lett. 7, 1638 (2016).

G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, and H. J. Snaith, Energy Environ. Sci. 7, 982 (2014).

N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok, Nature 517, 476 (2014).

J. Ma and L. W. Wang, Nano Lett. 15, 248 (2015).

G. W. ’t Hooft, Appl. Phys. Lett. 39, 389 (1981).

P. J. Bishop, M. E. Daniels, B. K. Ridley, and K. Woodbridge, Phys. Rev. B 45, 6686 (1992).

F. Stern, IEEE J. Quantum Electron. 9, 290 (1973).

C. H. Swartz, M. Edirisooriya, E. G. LeBlanc, O. C. Noriega, P. A. R. D. Jayathilaka, O. S. Ogedengbe, B. L. Hancock, M. Holtz, T. H. Myers, and K. N. Zaunbrecher, Appl. Phys. Lett. 105, 222107 (2014).

A. Kirk, M. DiNezza, S. Liu, X. H. Zhao, and Y. H. Zhang, in 39th IEEE Photovoltaic Specialists Conference (PVSC) (IEEE, 2013), pp. 2515–2517.

X. H. Zhao, M. J. DiNezza, S. Liu, S. Lin, Y. Zhao, and Y. H. Zhang, J. Vac. Sci. Technol. B 32, 040601 (2014).

T. Trupke, M. A. Green, P. Würfel, P. P. Altermatt, A. Wang, J. Zhao, and R. Corkish, J. Appl. Phys. 94, 4930 (2003).

W. Gerlach, H. Schlangenotto, and H. Maeder, Phys. Status Solidi A 13, 277 (1972).