Impact of Cation Multiplicity on Halide Perovskite Defect Densities and Solar Cell Voltages

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ABSTRACT

Metal-halide perovskites feature very low deep-defect densities, enabling thereby high operating voltages on solar cell level. Here, by precise extraction of their absorption spectra, we find that the low deep-defect density is unaffected when Cs^+ and Rb^+ are added during the perovskite synthesis. By comparing single-crystals and polycrystalline thin-films of methyl ammonium lead iodide/bromide, we find these defects to be predominantly localized at surfaces and grain boundaries. Furthermore, for the most important photovoltaic materials, we demonstrate a strong correlation between their Urbach energy and open-circuit voltage deficiency on the solar cell level. Via external quantum yield photoluminescence efficiency measurements, we explain these results as a consequence of non-radiative open-circuit voltage losses in the solar cell. Finally, we define practical power conversion efficiency limits of solar cells by taking into account the Urbach energy.

TOC GRAPHICS

Metal halide perovskites are promising photovoltaic materials thanks to their excellent optoelectronic properties,^{1,2} particularly their very low deep-defect density.³ Such characteristic translates in relatively low non-radiative recombination losses. Therefore perovskite solar cells (PSCs) maintain high densities of photo-generated carriers, and thus large quasi-Fermi level splitting, resulting in high operating voltages.⁴

Earlier, to gain insight into these optoelectronic properties, we investigated the optical absorption spectra of methylammonium lead iodide (MAPbI₃) perovskites, and found a sharp onset of their absorption coefficient, α , as well as a steep exponential slope of their sub-bandgap absorption edge E_U , often referred to as the Urbach energy, expressed by^{5,6}

$$\alpha(E) = \alpha_0 \exp\left(\frac{E-E_C}{E_U}\right), \quad (1)$$

where E is the photon energy, and α_0 and E_C are material constants. A low value of E_U (in the order of 10 meV) is a signature of high structural order of the material,⁷ which usually implies excellent electronic properties. Earlier, we established an empirical relation how low E_U values enable a low voltage deficiency at open-circuit conditions ($W_{OC} = E_G/q - V_{OC}$, with E_G the bandgap, q the elementary charge, and V_{OC} the open-circuit voltage). The exponential absorption/Urbach tail is an indication of imperfections in the crystalline ordering, given by defects and lattice vibrations. Generally, E_U can be accurately described by two additive components:^{8,9}

$$E_U(T) = E_U(0) + \frac{2E_U(0)}{\exp(E_P/kT)-1}. \quad (2)$$

where $E_U(0)$ is the temperature-independent, *static* part of E_U ; its value scales with the density of defects. The second term in (2) is the *dynamic* part of E_U , describing the contribution of electron-phonon scattering to the measured value of the E_U . In this term, T is the absolute sample temperature, k is the Boltzmann constant and E_P is the energy of the phonon involved in the

above-mentioned interaction in the single-phonon energy approximation.¹⁰ Recently we explored this relation and found an $E_U(0)$ value of about 3.8 meV for thin, polycrystalline MAPbI₃ films;¹¹ remarkably, this is smaller than that of well-established monocrystalline semiconductors such as Si,¹² GaAs,¹³ InP,¹⁴ or GaN,¹⁵ which underlines the excellent intrinsic optoelectronic properties of perovskite films.

To further investigate the remarkable absorption properties of metal halide perovskites, we study here perovskites with different halide and cation compositions since such perovskites, using appropriate cation and halide ratios, provide high processing reproducibility, improved phase stability, and bandgap tunability.^{16–19} On the other hand, single-crystal and thin-film forms of metal-halide perovskites show distinct characters at their surfaces and bulk, as shown previously.²⁰ Therefore, understanding the defect density for single-crystal and thin-film perovskites has critical importance in developing mitigation strategies for such defects. Here, to this end, the role of surface and bulk recombination, single-crystals MAPbI₃ and MAPbBr₃ were investigated. From the measured temperature dependence of E_U , we find that electronically-active defects in halide perovskites are situated mainly at the surface. We also find that the very low defect density remains unaffected by Cs⁺ and Rb⁺ addition to the perovskite system, explaining the photovoltaic performance of this material in the final solar cell. Finally, we discuss fundamentally the universal correlation between W_{oc} and E_U and for mixed-cation, mixed-halide perovskites specifically.

Results and discussions

To understand the role of the halide perovskite film composition on the defect structure and its correlation with E_U , we have studied a series of thin-film metal-halide perovskite samples by varying their cation (MA, FA, Cs, Rb) and halide (I, Br) compositions. To be able to discriminate surface from bulk properties, we fabricated the ‘classic’ MAPbI₃ and MAPbBr₃ compositions both in their thin-film and single-crystal forms (SC MAPbI₃ and SC MAPbBr₃). Next, we probed FA_{0.6}MA_{0.4}(PbI_{0.83}Br_{0.17})₃ thin films first without and then with additions of 7% Cs and 3 % Rb [denoted as Cs_{0.07}Rb_{0.03}(FA_{0.6}MA_{0.4})_{0.9}(PbI_{0.83}Br_{0.17})₃], as such sophisticated compositions have reportedly led to better material homogeneity and enhanced solar cell performance.^{16,17,21} Detailed descriptions of sample preparations and topological properties of the films are given in SI.

Here, we aim at comparing these materials and finding a fundamental understanding for the superior performance of mixed-cation, mixed-halide perovskites. To do so, we utilized photoluminescence (PL) micro-spectroscopy by which absorption coefficients over 15 orders of magnitude can be acquired, which is several orders of magnitude higher in sensitivity compared to other techniques such as PDS (4 orders of magnitude),⁵ FTPS (up to 7 orders of magnitude)²² and transmission/reflection measurement (typically only 2 orders of magnitude). Thanks to this, E_U values can be extracted with unprecedented precision, leading to an accurate evaluation of important material parameters, such as the deep-defect density or phonon energy. Moreover, this technique is well-suited to extract temperature-dependent absorption data which is not practical or even possible with other techniques.²³

Fig. 1 plots the temperature dependency of E_U for all probed perovskite thin films and single crystals by PL micro-spectroscopy. The studied thin films are polycrystalline in nature, consisting of sub-micrometer grains. To acquire E_U values, firstly we measured the temperature dependence of the PL spectra of all materials, then we used the reciprocal theorem to convert the PL data into absorption spectra similar to our previous study (see supplementary information).¹¹

Fig. 1: The temperature dependence of E_U for MAPbI₃ and MAPbBr₃ thin films and single crystals together with FA_{0.6}MA_{0.4}(PbI_{0.83}Br_{0.17})₃ and Cs_{0.07}Rb_{0.03}(FA_{0.6}MA_{0.4})_{0.9}(PbI_{0.83}Br_{0.17})₃ thin films. The lines are the fits of **Equation (2)**. The inset shows the static part of E_U , *i.e.* density of active defects for all the probed halide perovskites films and crystals, values fitted from **Equation (2)**.

The observed trends in **Fig. 1** give important hints about the characteristics of the materials. Firstly, the MAPbI₃ thin-film and single-crystal data, as well as results on MAPbBr₃ samples, show very similar E_U values throughout the whole scanned temperature range. Therefore, also the static Urbach energy $E_U(0)$ – representative for the density of electronically active defects in the material – calculated from **Equation (2)** are almost identical for thin film and single crystal of given material, see inset in **Fig. 1** and **Table 1**. Since perovskite single crystals usually have a

thickness of several hundreds of micrometers, whereas thin films are on the sub-micrometer scale, the surface-to-bulk ratio is several times higher for thin-film perovskites compared to single-crystal perovskites. Effective carrier lifetimes, τ_{eff} , for non-passivated MAPbI₃ thin films are in the order of 10 - 300 ns,^{2,24-26} in case of MAPbI₃ single crystals the τ_{eff} is higher, typically 1 – 150 μ s.^{3,27-29} A similar difference of two order of magnitude is documented for Br-based single crystals and thin films.^{30,31} Quite generally, $1/\tau_{eff} = 1/\tau_{bulk} + 2S/W$, with S the surface recombination velocity, and W the sample thickness (assuming identical surfaces on both film sides and relatively low S values). Based on the fact that for both iodine/bromine thin films and single crystals comparable E_U is measured, we may hypothesize that both feature comparable bulk defect densities (and therefore similar τ_{bulk}). This implies that the defect states responsible for the specific τ_{eff} values predominantly must be sought at the surfaces.^{20,30,31} This point highlights the urgency for the improvement of surface and interface quality of metal halide perovskites for better optoelectronic devices, since the poly-crystalline nature does not bring a significant drop in the bulk electronic quality. Highly effective surface passivation may increase the τ_{eff} of thin films to the level of 5 μ s,¹ comparable with MAPbI₃ single-crystal values.^{3,27-29}

Secondly, we can directly access phonon energies of probed materials, see **Table 1**. Its low value in case of halide perovskites³²⁻³⁵ is responsible for the weak temperature conductivity and may be important for many optoelectronic applications; infra-red lasers are one of the examples.^{36,37} The phonon energies are calculated in the single phonon approximation described by **Equation (2)** and summarized in **Table 1**. The fitted phonon energy of MAPbBr₃ film and SC is, despite the large error, lower compared to that of MAPbI₃ once, as may be deduced directly from different slopes of the respective temperature dependencies. But this trend is not in line with the

measured phonon energies of these materials for example by Raman spectroscopy.^{32–35} It means that the one phonon approximation is not able to fully describe the complex phonon spectrum of halide perovskites and the electron phonon scattering process. This uncertainty may affect $E_U(0)$ as well, we will take it into count when the absolute $E_U(0)$ values will be discussed. Measurement errors were evaluated based on several temperature measurement on MAPI films, see SI for more details.

Table 1: Phonon energy, static Urbach energy $E_U(0)$ values obtained from the temperature dependency of $E_U(T)$. Optimized open-circuit voltage V_{OC} , minimal voltage deficiency W_{OC} , external quantum yield EQY and corresponding non-radiative losses $|\Delta V_{OC}|$ for probed materials are summarized in the table. Solar cell with $\text{FA}_{0.6}\text{MA}_{0.4}(\text{PbI}_{0.83}\text{Br}_{0.17})_3$ was not prepared.

Sample	Phonon energy [cm ⁻¹]	$E_U(0)$ [meV]	V_{OC} [V]	W_{OC} [V]	EQY [%]	$ \Delta V_{OC} $ [mV]
SC MAPbI ₃	170 ± 30	4.9 ± 0.6	1.076 ²⁸	0.51	0.2 ± 0.02	168 ± 3
TF MAPbI ₃	155 ± 30	4.8 ± 0.6	1.16 ¹⁷	0.45	2.2 ± 0.2	98 ± 3
SC MAPbBr ₃	135 ± 30	4.7 ± 0.6	1.31 ³⁸	0.9	0.7 ± 0.08	129 ± 3
TF MAPbBr ₃	130 ± 30	4.6 ± 0.8	1.65 ³⁹	0.67	0.6 ± 0.06	134 ± 3
$\text{FA}_{0.6}\text{MA}_{0.4}(\text{PbI}_{0.83}\text{Br}_{0.17})_3$	130 ± 30	4.2 ± 0.6	NA	NA	14 ± 1	51 ± 3
$\text{FA}_{0.83}\text{MA}_{0.17}(\text{PbI}_{0.83}\text{Br}_{0.17})_3$ + 7 % Cs, 3 % Rb	120 ± 30	3.7 ± 0.6	1.105 ¹⁷	0.49	32 ± 3	30 ± 3

Thirdly, the E_U temperature dependencies remain, with substitution of MA^+ by FA^+ , as well as addition of Cs and Rb cations, almost unchanged. This implies that the E_U temperature dependencies are determined by electron scattering of phonons of similar energy in all cases. The fact that the phonon energy does not change with altering the cations in iodide films clearly proves the dominant role in the scattering process of vibrations of the cage (rather than that of

the cation captured within the cage).¹¹ More generally, this suggests that the electronic quality of halide perovskites is mainly given by the properties of the perovskite cage. The main role of the specific cation must then perhaps rather be sought in the crystal formation.¹⁷

Non-radiative recombination via deep-defect states can be the major source of performance losses in PSCs, especially in the absence of passivation strategies.^{4,40} Such recombination decreases the excess free electron- and hole-concentrations, which implies diminished quasi-fermi level splitting in the perovskite, and therefore lower operating voltages on device level. This effect is most notable as a reduction of the open-circuit voltage (V_{oc}) but also of the fill factor (FF) of in the solar cell. The importance of non-radiative recombination can be revealed through measurements of the external quantum yield (EQY), which is defined as a fraction of electron-hole pairs that recombine *radiatively*. The EQY is logarithmically proportional to the non-radiative losses $\Delta V_{oc}(non-rad)$ in finalized solar cells.^{4,40,41}

$$\Delta V_{oc}(non-rad) = -kT/q \ln(EQY), \quad (3)$$

where k is Boltzmann's constant.

With our experiments, we can plot the temperature dependence of the integrated PL intensity. The PL spectra were measured under identical optical settings for all temperatures; therefore the sensitivity of our set-up remains the same, and the obtained values are comparable, but on a relative scale. To connect these results with the optoelectronic quality of the probed perovskite films via non-radiative V_{oc} losses, we need to rescale the integrated PL intensity temperature dependence into the absolute scale, *i.e.* calculate the EQY temperature dependence. For this purpose, all the samples were characterized at room temperature by their EQY, see the

experimental section for a detailed description. The temperature dependencies of EQY are plotted for all characterized materials in **Fig. 2**.

Fig. 2: a) The temperature dependence of EQY for all the probed thin films and single crystals. b) EQY as a function of $E_U(0)$. The right axis of the graph is calculated from the EQY scale (is not independent) to show directly the non-radiative V_{OC} losses (**Equation 3**), as presumed in the finalized solar cell. Solid lines are guides for an eye (exponential fits of the dependencies), colored areas estimate the measurement error.

We found that the EQY decreases exponentially with temperature for all perovskites thin films and the SC MAPbI₃. This decrease, which is the so-called PL thermal quenching, is caused by the ‘opening’ of non-radiative recombination channels with increasing temperature.^{42–44} At low temperatures, below 200 K, the PL emission of thin-film perovskites saturates at very high values: In the case of Cs_{0.07}Rb_{0.03}(FA_{0.6}MA_{0.4})_{0.9}(PbI_{0.83}Br_{0.17})₃ this level is at 80% EQY. In general, we observe that the probability of non-radiative recombination is highly suppressed in lead halide perovskites at low temperatures. On one hand, the low probability stems from the very low

phonon energy: Indeed, with very low phonon energies, non-radiative recombination becomes by necessity a multi-phonon process, which reduces its probability, as is described in detail by Kirchartz *et al.*⁴⁵ The other effect is an exponential decrease of phonon density with sample cooling.

From **Fig. 1**, we can extract also $E_U(0)$, the static component of the Urbach energy, which directly corresponds to the number of deep defects states active in the electron scattering processes.^{8,9}

Fig. 2 b displays $E_U(0)$ for all probed materials. Earlier, we found that thin-film MAPbI₃ features a lower number of active static defects in comparison with standard high-quality bulk semiconductors such as crystalline Si (5.4 meV), GaAs (5.2 meV), and GaN (6.3 meV).¹¹ This extraordinary Urbach energy value may be explained by dynamic shortening of disorder potentials in anharmonic halide perovskites.⁴⁶ **Fig. 2 b** shows that this trend also holds for the other perovskites probed here. Interestingly, all the measured temperature dependences, except the MAPbBr₃ film and crystal, have very similar shape. It means that incorporation of FA⁺ as well as adding Cs⁺ and Rb⁺ does not lead to substantial increase of defect density in the perovskite film, as suggested by calculated low $E_U(0)$ values. Moreover, it seems that $E_U(0)$, the number of deep defects, scales with the measured EQE and with the predicted V_{OC} losses, see **Fig. 2 b**. However, since the measured data are very similar, the $E_U(0)$ trend based on simple one phonon energy model may originate from its inaccuracy. Nevertheless the increase of EQE with material complexity is in line with results,⁴⁷ where similar films were probed.

The measured EQY at room temperature scales with $E_U(0)$, as calculated from **Equation (2)**, see **Fig. 2 b**. For the iodide based thin films, the calculated $E_U(0)$ in single phonon approximation, *i.e.*

the density of deep defect states, decreases with adding Cs^+ and Rb^+ . Meanwhile, the EQY and the corresponding non-radiative V_{OC} losses decrease from 90 down to 30 *mV*. The values for SC MAPbI_3 and for the MAPbBr_3 film cannot be directly compared with the other iodide-based thin-film perovskites due to the following reasons: the SC MAPbI_3 is a bulk sample, therefore, the density of photo-generated charge carriers (and thus the radiative recombination) is lower in comparison with thin films. Surface passivation may be significantly different in case of thin-film MAPbBr_3 , which makes direct comparison with MAPbI_3 difficult. Both the above mentioned effects increase the non-radiative V_{OC} losses, in agreement with our measurement as shown in **Fig. 2b**. All these results are in line with the photovoltaic characteristics of the relevant devices that employ the listed perovskites (see **Table 1**),¹⁷ and also with other reports in literature.⁴⁸

Finally, we discuss the relationship between E_U and voltage losses, which we reported earlier.^{5,11} So far, this relation has been mainly empirical, and the fundamental origin for this observation was not clear. To this end, we have calculated the non-radiative losses for the materials probed here as well as the MAPbI_3 temperature dependence from Ref. ¹¹. Non-radiative losses for other (non-perovskite based) semiconductors are taken from literature.⁴⁰

Fig. 3: W_{OC} and non-radiative V_{OC} losses versus E_U for perovskites materials probed here, thin-film MAPbI₃ at low temperatures¹¹ and typical photovoltaic absorber materials (values are taken from^{13,40,49–53}). Shadowed area marks the region of V_{OC} losses from the SQ limit, whereas the lines in this area present the values calculated for semiconductors used in this study with the same color code.

Fig. 3 shows for all the plotted materials that the *slope* of the linear trend between overall voltage losses (W_{OC}) and E_U , originally retrieved from De Wolf *et al.*,⁵ is found to be very similar to the slope of the linear trend between the non-radiative V_{OC} losses and E_U . As can be seen in **Fig.3**, both the fitted slopes are almost identical. The vertical offset between these two lines is given by additional, fundamental/SQ voltage losses, originating from thermodynamics limits.⁴¹ The mean difference between the W_{OC} and the non-radiative V_{OC} is 280 mV, which is consistent with the theoretical predictions for standard solar irradiation (AM 1.5G, 1 sun, bandgap of 1.5 eV).⁴¹ It is important to note that E_U itself is changing the fundamental V_{OC} losses by changing the total number of absorbed photons in the active material.^{54,55} These fundamental losses are, however, order of magnitude less significant in comparison with our observation. The additional and more relevant effect reported here is given by non-radiative recombination on deep defects, detected indirectly by the broadening of the absorption edge, by the Urbach tail. To sum up: we can link the E_U value with the non-radiative V_{OC} losses via the deep-defect density in the semiconductors (*i.e.* the non-radiative recombination caused by these deep-defect states). By doing so we can estimate additional minimal voltage losses (beyond the SQ limit) based on Urbach energy:

$$\Delta V_{OC}^{non-rad}(E_U) = 10 E_U/q \approx V_{OC} - W_{OC}^{SQ\ Limit}, \quad (4)$$

where q is the charge of an electron (see supplementary material for voltage losses scheme). This first-order estimate will help to estimate the efficiency potential of newly developed materials based on the optical properties only, independent from the contribution of the other layers which can accelerate the development of new photovoltaic absorbers.

To conclude, we have found a very low density of recombination-active defects for all probed halide thin-films perovskites as well as single crystals. The comparison of E_U for bulk and thin-film MAPbI₃ suggests that these recombination centers are situated rather at the perovskite surface, which - from a device engineering perspective - mandates the further development of grain-boundary, surface and contact passivation strategies.⁵⁶

We have found clear evidence, beyond empiricism, that the linear correlation between the minimal V_{OC} losses for a given material and its Urbach energy is given mainly by the non-radiative recombination losses. In this way, we can predict the V_{OC} of the optimized solar cell with the newly developed active layers. And finally, even the most sophisticated films featuring mixed cations (FA, MA, Cs, and Rb) and mixed halides (I, Br) have extremely low density of active deep defect states comparable with MAPbI₃ thin films. This is well supported by the highest external luminescence quantum yield as well as the best solar cell properties (i.e the lowest non-radiative V_{OC} losses). Our findings explain the excellent performance of mixed cation halide perovskite, underlining the potential of perovskites in photovoltaics and optoelectronics applications.

Experimental Methods

PL spectra are measured using a HeCd 442 nm excitation laser in a Renishaw REFLEX micro-spectroscope. The intensity of the laser light is reduced to the equivalent of about 4 suns (i.e. $\sim 0.4 \text{ W/cm}^2$), in order to prevent any structural degradation occurring during measurements.³² The external quantum yield was measured by a homemade set-up based on the integrating sphere (diameter of 10 cm).⁵⁷ PL was excited by the blue laser 473 nm at room temperature. Laser intensity was adjusted with the neutral density filters to get the same illumination intensity as 1 sun (i.e. $\sim 0.1 \text{ W/cm}^2$). The PL temperature dependence was measured in the Linkam temperature stage. The EQY temperature dependence was calculated from absolute integral intensities measured with the temperature stage, rescaled to the absolute EQY values by comparison with the measurement at room temperature. Ice crystals occur during the measurement at temperatures lower than 200 K, this effect may lead to underestimation of the EQY at these conditions.

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Supporting Information Available

Supporting Information contains the description of samples/solar cells preparation, experimental methods section, the temperature dependence of the PL and absorption spectra, and bandgap temperature dependence for measured materials.

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Impact of metal-halide perovskite composition on Urbach Energy: from thin films to single crystals

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Experimental Methods

Sample preparation

The perovskite films were prepared with the 1-step process. The perovskite precursor was spun at 2000 rpm (acceleration 200 rpm/s), then 4000 rpm (acceleration 1000 rpm/s) for 25 s. Chlorobenzene was dripped the 10 s. prior to the end of the process for the antisolvent treatment step. The spin-coated films were immediately transferred to the hotplate and annealed at 100 °C for ~20 min. For the perovskite precursor, all the chemicals were used without any further purification. The organic cation salts methylammonium iodide (MAI), formamidinium iodide (FAI), methylammonium bromide (MABr), formamidinium bromide (FABr) were purchased from Dyesol, the lead halide compounds (PbI₂, PbBr₂), RbI and CsI were purchased from Sigma-Aldrich. For the precursors, 1 mL of the pristine FAMA solution (without any Cs or Rb additives) was prepared by dissolving 508 mg PbI₂ (99.99%, Sigma Aldrich); 80.7 mg PbBr₂ (99.99%, Sigma Aldrich); 159 mg of MAI (99.99%, Dyesol); 25 mg of FABr (99.99%, Dyesol) in the mixed solvent of DMF:DMSO (4:1 v/v). The FAMA solution was stirred at 60°C for 2 hrs and then at room temperature overnight. CsI (1.0 M) and RbI (1.0 M) solutions were prepared by dissolving RbI (99.99%, Alfa Aesar) and CsI (99.99%, Alfa Aesar) in DMF: DMSO (4:1 v/v). Precursor solutions with various Cs and Rb additions were prepared by adding an appropriate amount of CsI and/or RbI solutions to the MAFA solution. All thin films were 600 nm thick with similar grain size distribution.

Characterization Methods

The Photoluminescence spectra are measured using a HeCd 442 nm excitation laser in a Renishaw REFLEX micro-spectroscope. The intensity of the laser is reduced to the equivalent of about 4 suns. The PL measurements are performed on MAPbI₃, MAPbBr₃, FA_{0.6}MA_{0.4}(PbI_{0.83}Br_{0.17})₃ and Cs_{0.07}Rb_{0.03}(FA_{0.6}MA_{0.4})_{0.9}(PbI_{0.83}Br_{0.17})₃ thin films deposited on a glass substrate, as well as on MAPbI₃ and MAPbBr₃ single crystals. In the following text, the CH₃NH₃⁺ (methylammonium) and CH(NH₂)₂⁺ (formamidinium) cations are denoted as MA and FA respectively. For measurements of the photoluminescence temperature dependence, we use a Linkam temperature stage THMS600.

Photoluminescence absorption spectra

Taking advantage from the reciprocity of the relation between the PL and absorption spectra the absorption spectra was calculated using generalized Plancks law (S.1) for a photon current density $dj_e(h\nu)$ per energy interval.

$$dj_e(h\nu) \approx A_{BB}(h\nu)(h\nu)^2 \exp\left(-\frac{h\nu}{k_B T}\right), \quad (\text{S.1})$$

where $h\nu$ is the photon energy, A_{BB} is the band-to-band absorptance, k_B is the Boltzmann constant and T is the absolute temperature.¹ In order to obtain the temperature dependence of the Urbach energy $E_U(T)$ first, temperature dependence of PL spectra was measured. Secondly, using the equation (S.1) the absorption spectra at given temperature was computed and as a last step the absorption spectra were fitted by the Urbach's rule (S.2)²

$$\ln(A_{BB}(h\nu, T)) = \ln(A_{BB0}) + h\nu \frac{1}{E_U(T)}. \quad (\text{S.2})$$

The fit was performed on the absorptance interval between 5% and 0.001% of absorptance. The temperature dependence $E_U(T)$ was subsequently fitted by equation (S.3) giving us the information about static part of the Urbach energy E_{Stat} and average energy of phonon excitations $h\nu_p$.³

$$E_U(T) = E_{Stat} + \frac{2E_{Stat}}{\exp\left(\frac{h\nu_p}{k_B T}\right) - 1}, \quad (\text{S.3})$$

where $E_{Stat} = \frac{h\nu_p}{2\sigma_0}$. The results for studied samples are shown in Table S.1. The values of the E_{Stat} are very low and lies in the range from 3.5 to 4.9 meV. The samples containing bromide tends to have slightly lower E_{Stat} and average phonon energy $h\nu_p$ in comparison with purely iodide samples.

Fig. S1: The temperature dependence of normalized photoluminescence of MAPbI₃ thin layer (left) and the same dependence of calculated absorbance (right).

Fig. S2: The temperature dependence of normalized photoluminescence of MAPbI₃ single crystal (left) and the same dependence of calculated absorbance (right).

Fig. S3: The temperature dependence of normalized photoluminescence of MAPbBr₃ thin layer (left) and the same dependence of calculated absorbance (right).

Fig. S4: The temperature dependence of normalized photoluminescence of MAPbBr₃ single crystal (left) and the same dependence of calculated absorbance (right).

Fig. S5: The temperature dependence of normalized photoluminescence of FA_{0.6}MA_{0.4}(PbI_{0.83}Br_{0.17})₃ thin layer (left) and the same dependence of calculated absorbance (right).

Fig. S6: The temperature dependence of normalized photoluminescence of $\text{Cs}_{0.07}\text{Rb}_{0.03}(\text{FA}_{0.6}\text{MA}_{0.4})_{0.9}(\text{PbI}_{0.83}\text{Br}_{0.17})_3$ thin layer (left) and the same dependence of calculated absorbance (right).

Bandgap energy

The bandgap energy was determined from the photoluminescence spectra by finding the center of a photoluminescence peak at half of its maxima, see Fig. S7. On the Fig. S8 there are shown the temperature dependences of the bandgap energy for all studied samples. The pure bromide and iodide thin films show a linear decrease in the bandgap energy with temperature. These changes correspond to the phase transitions of structures from cubic to tetragonal at $T \approx 234$ K and from tetragonal to orthorhombic at $T \approx 145$ K for MAPbBr_3 and from tetragonal to orthorhombic at $T \approx 160$ K for MAPbI_3 .⁴ The E_{Gap} of the mixed samples is increasing with the decreasing temperature up to $T \approx 230$ K. With further decreasing of the temperature the E_{Gap} linearly decreases with temperature.

Fig. S7: Normalized photoluminescence spectrum of $\text{Cs}_{0.07}\text{Rb}_{0.03}(\text{FA}_{0.6}\text{MA}_{0.4})_{0.9}(\text{PbI}_{0.83}\text{Br}_{0.17})_3$ measured at 300 K.

Fig. S8: Optical bandgap energy temperature dependence. The values were obtained as an energy corresponding to the center at half maximum of the photoluminescence peak.

Fig. S9: Description of the voltage losses in the solar cell as discussed and designated in the main manuscript.

Repeatability and standard deviation

We have repeated the temperature measurement of Urbach energy several times, all the results for MAPI samples are summarized in Figure 10. The measured Urbach energies are almost identical even if we have used different samples, newly deposited once as well as perovskite films partially degraded in a humid atmosphere. We are not able to compare the sample properties before and after the measurement. The sample is partially covered by ice at low temperatures and once it is heated up the ice melts and the film is fully degraded after the measurement.

Fig. S10: The temperature dependence of the Urbach energy for five MAPI samples.

We have evaluated the static part of Urbach energy (Fig. 11) and the energy of the phonons involved in the electron-phonon scattering process (Fig. 12) for all the measured temperature series. Based on this analysis, we have assumed the errors for all the measured data.

Fig. S11: The static Urbach energy component of five different MAPI samples. The red area shows calculated statistical error (one sigma). The final estimated error for static Urbach energy was 0.4 meV, taking into count other possible deviations.

Fig. S12: Phonon energy of MAPI films for five independent temperature measurements. The red area shows calculated statistical error (one sigma). The final estimated error for phonon energy was 30 cm⁻¹, taking into count other possible deviations.

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