Impact of band structure on recombination and efficiency in halide perovskite solar cells close to the radiative limit

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Abstract

Some metal-halide perovskites have exceptionally good optoelectronic properties that make the materials attractive for applications in photovoltaics and other optoelectronic applications. Among the most remarkable properties are the extremely long charge-carrier lifetimes and high open-circuit voltages that are observed in thin films of $CH_3NH_3PbI_3$. Recently, several explanations have been brought forward that connect the high lifetimes and V_{oc}s with peculiar properties of the band structure of perovskites, in particular (i) the combination of a direct and an indirect band gap with a small energy offset and (ii) the low effective density of states. Here, we show how the direct-indirect combination of band gaps can indeed lead to longer lifetimes but the recombination rate, which is proportional to the ratio of the equilibrium carrier concentrations and the lifetime is likely to remain constant or constant. Therefore, the direct-indirect combination can explain good charge carrier collection but not high open-circuit voltages. This is different for the second feature of the band structure, namely the low effective density of states, which is combined with a high absorption coefficient. This is only possible of the matrix transition elements are high in perovskites. While for a given absorption coefficient, the effective density of states is irrelevant in the radiative limit at high mobilities, this is not the case if non-radiative recombination is present. This means, the high absorption at low densities of states can indeed help the open-circuit voltage.

Introduction

Based on the early findings of its sharp absorption edge, $CH_3NH_3PbI_3$ (MAPI) was initially considered to have a direct band gap. This finding was recently questioned by reports[1,2] that present evidence for an indirect band gap just below the direct one (in a distance of roughly 2 to 3 kT). Because radiative transitions via the indirect band gap are usually much slower than via the direct gap, one could argue that such a configuration should increase charge carrier lifetimes and therefore the open-circuit voltage. However, especially in the radiative limit, such an explanation would be incompatible with earlier findings that provide mathematical proof[3,4] for the fact that a step function is the ideal shape for the absorptance of a solar cell. These proofs work in the radiative limits at high mobilities, i.e. in the situation that is described by the Shockley-Queisser[5] model.

Another related aspect that makes these findings particularly interesting is the question of selection metrics in numerical materials screening for photovoltaics. One of the typically used selection metrics is designed such that an indirect transition below a direct one is considered harmful for anticipated photovoltaic performance and those materials are therefore discarded (or considered less useful) by the algorithm.

Results and Discussion

We performed drift-diffusion simulations including photon recycling as described previously.[6] The efficiency as a function of mobility is shown in Figure 1. Here, we changed the position of the indirect band gap relative to the direct one, from 10 meV to 100 meV. In all cases, the absorption via the direct band gap was kept low. We see that in the high mobility limit, the smallest shift gives the highest efficiency, consistent with the earlier findings that a step function is always best in the radiative limit at high mobilities. Towards lower mobilities, the indirect band gap starts to help due to the enhanced radiative lifetimes. This means that the

fill factor is controlled by the mobility-lifetime product or variations thereof.[7] However, the open-circuit voltage is controlled by

$$B_{\text{eff}} n_0 p_0 = \int (\alpha_i + \alpha_d) \phi_{bb}(E) dE \quad . (1)$$

where B_{eff} is the effective radiative recombination coefficient, n_0 and p_0 are the equilibrium concentrations, α_i and α_d are the direct and indirect absorption coefficient and ϕ_{bb} is the black body spectrum as a function of energy E. While B_{eff} might be reduced by adding the indirect band gap, $B_{\text{eff}} n_0 p_0$ is not and so V_{oc} remains constant or even goes down. This implies that energy can be spent to improve charge collection such as in a bulk heterojunction device but it is not possible to improve V_{oc} by that.

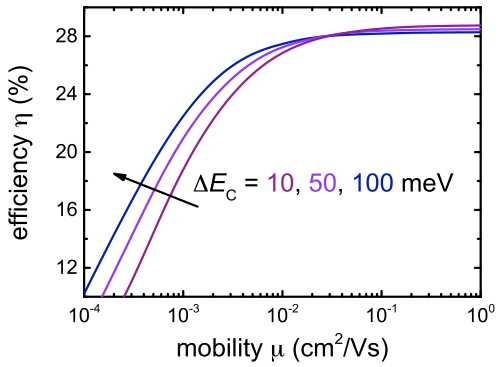

Figure 1: Efficiency as a function of mobility for a series of energy shifts ΔE_C between the direct and the indirect band gap.

When trying to fit the actual absorption coefficient of MAPI and more importantly the product of afbb using the normal equations for absorption coeffiicents for direct and indirect transitions, it appears (see Fig. 2) that the indirect transition dominates the r.h.s of Eq. (1) and therefore radiative recombination. This means it is questionable whether even the effect shown in Fig. 1 would be obtained in MAPI.

Improving efficiency in the radiative limit can essentially only be done by optimizing the band gap and by making the absorptance more step-function like. However, away from the radiative limit, other quantities become important. Especially the internal and external LED quantum efficiencies become relevant when going away from the radiative limit. In order to improve the internal LED quantum efficiency, one way would be to improve the electron-photon coupling relative to the electron phonon coupling. This would lead for instance to lower values of $n_0 p_0$ for a constant band gap and absorption coefficient, which could indeed improve the LED quantum efficiency and bring V_{oc} closer to its radiative limit.

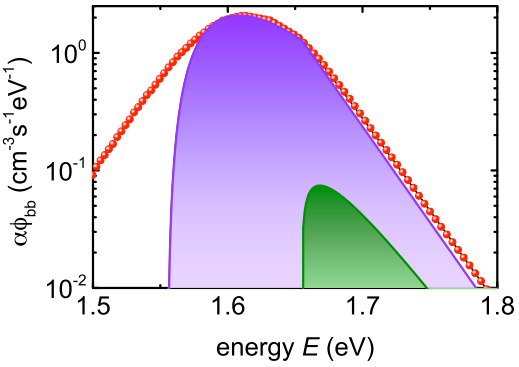

Figure 2: The product of absorption coefficient and black body spectrum that controls the radiative recombination rate for a MAPI device (red symbols, data taken from ref. [8]) and a possible fit to the data using a direct (green) and an indirect absorption coefficient (blue). In this case, the indirect transition would dominate radiative recombination.

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