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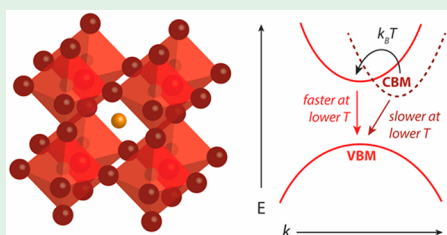
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Thermally Activated Second-Order Recombination Hints toward Indirect Recombination in Fully Inorganic CsPbI₃ Perovskites

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S Supporting Information



ABSTRACT: The relationship between the dipole moment of the methylammonium cation and the optoelectronic properties of lead halide perovskites remains under debate. We show that both the temperature-dependent charge carrier mobility and recombination kinetics are identical for methylammonium and cesium lead iodide, indicating that the role of the monovalent cation is subordinate to the lead iodide framework. From the observation that for both perovskites the electron–hole recombination is thermally activated, we speculate that the bandgap is slightly indirect.

Application of lead halide perovskites with the general structure ABX₃ in solar cell devices yields efficiencies close to 23%.¹ This is attributed to the combination of high absorption coefficients, sufficiently high charge carrier mobilities, and long lifetimes, enabling efficient collection of excess charges. Previous work on methylammonium lead iodide or bromide (MAPbX₃) has shown that these long lifetimes could be related to the presence of the Rashba effect, resulting in a slightly indirect bandgap.^{2–8} Importantly, optical excitation of charges still predominantly occurs via direct transitions, while recombination involves an indirect transition. However, it has remained under debate whether these effects are related to the dipole moment of the organic cation.

In this work, we show that both the temperature-dependent mobility and recombination kinetics in CsPbI₃ follow the same trend as in MAPbI₃. Importantly, in both cases, the second-order recombination of free charges is thermally activated, consistent with an indirect recombination pathway.⁷

The CsPbI₃ films are prepared using physical vapor deposition, yielding metastable orthorhombic black-phase CsPbI₃.^{9–11} Figure 1 shows intensity-normalized Time-Resolved Microwave Conductivity (TRMC) traces recorded at 293, 260, and 220 K, for charge carrier densities in the regime

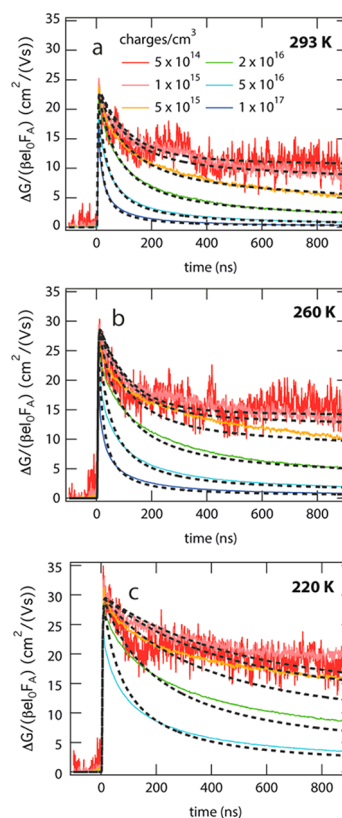


Figure 1. TRMC traces for vapor-deposited black-phase CsPbI₃, recorded at 293 K (a), 260 K (b), and 220 K (c) for initial charge carrier densities of 5×10^{14} to 10^{17} cm^{-3} . The modeled traces are added as black dashed lines.

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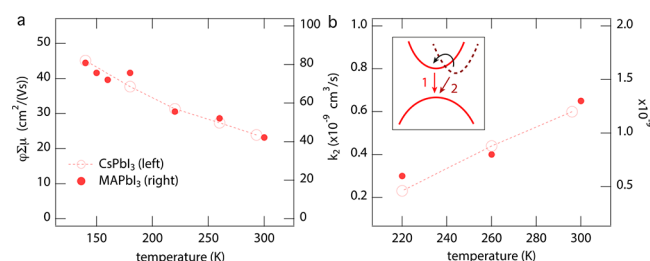


Figure 2. Effective mobility $\varphi \Sigma \mu$ (a) and k_2 (b) as a function of temperature for CsPbI₃ (open circles, left axis) and MAPbI₃ (closed circles, right axis, data from ref 7). The dotted lines between the open circles are added to guide the eye.

between 10^{15} and 10^{17} cm⁻³. From the maximum signal height, we deduce that the room-temperature mobility is around 25 cm²/(V s).¹⁰ Interestingly, on decreasing the temperature, the mobility in CsPbI₃ gradually increases, following a temperature-dependent trend similar to that observed for MAPbI₃ (see Figure 2a) given by $\mu \propto T^{-1.5}$.^{7,12} This shows that the charge carrier mobility in lead iodide perovskites is mainly limited by phonon scattering,⁷ independent of the monovalent cation. Remarkably, not only the mobility but also the lifetime of mobile charges follows the same temperature dependence as that of MAPbI₃. That is, for a range of excitation densities between 5×10^{15} and 10^{17} cm⁻³, the lifetime is enhanced on lowering the temperature. Because this corresponds to a regime in which the lifetime decreases with increasing initial charge carrier densities, we can conclude that higher-order recombination is retarded with decreasing temperatures. Below 5×10^{15} cm⁻³, the lifetime is not dependent on the excitation density, indicating a first-order process such as trap-assisted recombination.

To quantify this, we fitted the experimental data at 220 K < T < 300 K using our previously described kinetic model (Figure S2),¹³ as shown by the dashed lines in Figure 1. The kinetic parameters are listed in Table S1. In Figure 2b, the second-order recombination rate (k_2) is plotted for CsPbI₃ with values previously found for MAPbI₃.⁷ Importantly, although the absolute values are different, in both cases the k_2 at 220 K is less than half its room-temperature value. This is in contrast with the temperature-dependent trend in recombination rate typically found in direct semiconductors and previously reported for MAPbI₃ at high fluence ($>10^{17}$ cm⁻³),^{12,14,15} which is several orders of magnitude higher than the charge densities presented here. Although these previous reports^{12,15} suggest that direct recombination dominates at higher charge densities, our results show that in both CsPbI₃ and MAPbI₃, second-order recombination is actually a thermally activated process for charge densities ranging from 10^{15} to 10^{17} cm⁻³. Previously, we hypothesized that this was due to the conduction band minimum being slightly shifted in k -space from the valence band maximum,⁷ resulting in an indirect bandgap from which recombination is momentum-forbidden. In addition, the high absorption coefficients¹⁰ indicate the presence of a direct transition. The origin of the thermally enhanced recombination rates may therefore be twofold: (1) thermal energy releases electrons from the CBM to a state from which direct recombination is possible and (2) the electrons decay from the CBM to the VBM via indirect recombination on interacting with a phonon, see inset in Figure 2b. The present observations suggest that the indirect recombination pathway is not related to (collective) orientations of methylammonium dipoles.

We note that the increased lifetime observed upon lowering the temperature is not related to reabsorption of emitted photons. That is, the external photoluminescence quantum efficiency (PLQE) in CsPbI₃ is far below 1%.¹⁰ Even in the case of very poor output coupling and a 10-fold increase in PLQE on lowering the temperature (see Figure S1), still more than 95% of the second-order recombination is nonradiative and therefore cannot be reabsorbed. Additional scenarios to explain the thermally enhanced recombination include charge immobilization into shallow traps or the formation of large polarons. However, because both of these do not satisfactorily explain the experimental temperature-dependent mobility following $T^{-1.5}$,^{7,16} these are in our opinion unlikely to dominate the charge carrier recombination properties. Instead, the combination of increasing mobility and retarded second-order recombination on decreasing the temperature suggests an indirect recombination pathway for mobile charges. The low PLQE indicates that the second-order recombination between mobile charges is mainly nonradiative, which could mean that indirect recombination does not result in the emission of a photon. Most importantly, our present results show that both the temperature-dependent mobility and recombination mechanism are fully dominated by the lead iodide framework instead of the dipole moment of the organic cation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b01106.

Additional figures and experimental methods (PDF)

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Notes

The authors declare no competing financial interest.

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