Title:	ETURN TO ISSUEPREVC: SPECTROSCOPY AND ...NEXT Cation-Dependent Hot Carrier Cooling in the Lead-Free Bismuth Halide A3Bi2I9 (A = FA, MA, and Cs) Perovskite
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Keywords:	Cation-Dependent Lead-Free
Issue Date:	2021
Publisher:	ACS Publications
Citation:	The Journal of Physical Chemistry C, 125(18), 9891–9898.
Abstract:	Lead-free halide perovskites, as environment-friendly materials, have received critical interest in photovoltaic applications. In this regard, the bismuth halide perovskites demonstrate better stability under ambient conditions than lead halide perovskites and consequently remain one of the critical areas for the development of lead-free absorber materials. The steady-state optical properties are widely investigated in these bismuth halide perovskites, but excited-state charge carrier dynamics such as hot carrier relaxation remain elusive. However, it is crucial to investigate the rapid relaxation of above band gap “hot” carriers as it restricts the fundamental efficiency limit in the perovskite solar cells. Here, we demonstrate the cation-dependent hot carrier cooling in the lead-free A3Bi2I9 [A = FA (formamidinium), MA (methylammonium), and Cs (cesium)] perovskite by using femtosecond transient absorption spectroscopy. These lead-free perovskites were fabricated from gamma-butyrolactone (γ-GBL) solvent to ensure uniformity and continuity of the as-grown film and were well characterized by XRD, SEM, and steady-state absorption and photoluminescence spectroscopy. With varying A-cations, we observe that the hot-hole relaxation is slowest in the all-inorganic perovskite Cs3Bi2I9 (12.83 ps) and hot electron relaxation is slowest in the hybrid MA3Bi2I9 perovskite (6.42 ps) at the same excitation energy. The observed strong dependence of carrier cooling on cation composition is explained by the interaction between the different organic cations (A = FA, MA, and Cs) with the Pb–Br frameworks. Our study provides an opportunity to understand the effect of cations on the excited-state carrier dynamics, especially the hot carrier relaxation in the bismuth halide perovskites. This will pave the way for designing hot carrier-based high-efficient lead-free perovskite photovoltaic devices.
Description:	Only IISER Mohali authors are available in the record.
URI:	https://pubs.acs.org/doi/10.1021/acs.jpcc.1c01509 (https://pubs.acs.org/doi/10.1021/acs.jpcc.1c01509) http://hdl.handle.net/123456789/5012 (http://hdl.handle.net/123456789/5012)
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