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Title:	Tracking The Ultrafast Photophysical events in all Inorganic Metal Halide Perovskites through Transient absorption Spectroscopy
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Keywords:	Tracking The Ultrafast Photophysical Transient absorption Spectroscopy Inorganic Metal Halide Perovskites
Issue Date:	Mar-2023
Publisher:	IISER Mohali

Abstract:

Back in the year 2013, Metal Halide Perovskites (MHPs) made their first debut in the photovoltaic (PV) research world by showcasing an impressive Photo-Conversion Efficiency (PCE) of 3.8%. Since then there has been no turning back; in fact there has been a commendable hike in these numbers and lately these figures have skyrocketed to 31.25 % in case of organic-inorganic perovskite based tandem cells. All this may be attributed to their unique properties like defect tolerance, relaxed carrier cooling, large diffusion lengths etc. to name a few. However, the situation is different with the all-inorganic MHPs since their status in the PV business is not very spectacular and the resultant PCEs lag behind their hybrid counterparts. Despite this, the all-inorganic MHPs are still chosen over hybrid ones because of their greater stability and long-term consistency. It is moreover anticipated that these materials may attain their theoretically projected device efficiency limitations provided the necessary efforts are made to unleash them from their shortcomings. In addition to optimising any device structure for improvising the performance, understanding the sequence of the photophysical events that occur in the functional layer subsequent to photoexcitation is equally vital. This thesis is based on comprehensively examining these lesser known fundamental photophysics and the ultrafast excited state occurrences in both lead based and lead free all-inorganic MHPs as well their heterostructures. For serving this goal, femtosecond transient absorption (TA) spectroscopy is deployed as a valuable asset. Because of the ultrashort pulsewidths, the time scales that may be analysed with this method typically vary from a few femtoseconds (fs) to nanoseconds (ns). In this way by leveraging the advantages of TA spectroscopy, we have attempted to track down the transient response of the photogenerated entities such as charge carriers, excitons, and other quasi-particles that form and decay across these time scales in our systems of interest. Besides this, we have also probed some of the MHP systems at cryogenic temperatures to better understand the phonon aided phenomena which ultimately drive the carrier dynamics by mitigating the thermal complications that otherwise interfere at room temperature. □ Slow carrier cooling is advantageous for PV applications and if strategically harnessed, can assist in achieving high PCEs. The first work is designed with an aim to further retard the carrier relaxation rate in the prototypical CsPbBr₃ system which is already known to exhibit slow cooling. For accomplishing this aim, we provided an envelope of highly polar Cs₄PbBr₆ over CsPbBr₃ core (Type 1 structure) and found that as per our anticipation the carrier cooling dynamics demonstrated by this core-shell configuration is much retarded than the pristine CsPbBr₃. Further upon examining the dynamics of the low energy region, we discovered that the Type-1 architecture is not the only factor contributing to the delayed carrier cooling observed here; polaron formation is also equally liable. The mobility of the carriers that are photo-generated in the shell is fairly low due to the formation of polarons in the highly polar Cs₄PbBr₆ lattice. Even though these carriers are native to the Cs₄PbBr₆ shell, they eventually relax at the CsPbBr₃ band edges, which delays the cooling of the carriers even further, as shown by the kinetics probed at the CsPbBr₃ bleach position. □ The second project which is based on temperature-dependent investigations, executed for CsPbBr₃ revealed that while the carrier cooling dynamics are rather sluggish at 300 K, they are seen to be expedited when the lattice temperature is gradually lowered to 5 K. We identified the cause of such accelerated kinetics to be the inability of CsPbBr₃ lattice to sustain the polarons at low temperatures because of the absence of longitudinal optical (LO) phonons. However, due to the abundance of LO phonons at temperatures in the proximity of 300 K, the indulgence of polaron brought on by strong carrier-LO phonon coupling in the carrier cooling process manifests as slow kinetics at temperatures close to 300 K. Since the devices while in operation are subjected to various temperature settings, this prior understanding of the hot carriers' typical behaviour may be utilised to optimise the performance of CsPbBr₃ based device. □ Apart from the utility in PV domain, CsPbBr₃ employed in conjunction with PbS in a composite system is known to function as a highly sensitive, broadband photodetector. The third work has been designed to explore the underlying hot carrier relaxation and transfer strategies within the CsPbBr₃-PbS heterostructure. For this intent, we vigilantly chose a set of different excitation energies. While exciting with high energy photons (300 nm) and comparing the bleach growth kinetics, we found the transfer of the hot carriers in this Type-1 heterostructure to be bi-directional since the bleach growth dynamics are noticed to be quite decelerated in contrast to those monitored for the pure NCs. However, there is a drastic variation observed when the composite is excited close to the band edge. The probe dynamics in such instance of near band gap excitation (480 nm), suggests that unlike the hot carriers, the cold carriers on the other hand tend to opt for only one way transfer of carriers, that is, from CsPbBr₃ to PbS energy states. Such a detailed knowledge of carrier relaxation and transfer mechanisms can prove utterly advantageous for the design and further improvement in the performance of any sort of photo electronic devices employing CsPbBr₃-PbS colloidal hetero-structure. □ The fourth project is based on the inspection of lead free Cs₂SnI₆ system which is a competing contender for the lead containing perovskite systems and has also shown promising results. Despite this, virtually little is known for this system. Employing TA spectroscopy, we have attempted to portray a real time picture of its phonon structure and identify the modes that were yet not assigned an origin particularly, the low frequency silent modes which are overlooked by the conventional spectroscopies. Additionally, we looked at the unified framework of dispersive excitation and impulsive scattering to examine the generation mechanism of the low symmetry modes observable in the frequency domain as well as the fully symmetric coherent phonon mode "A_{1g}" that is manifested as strong oscillations in the time domain data for Cs₂SnI₆. The excitation pump phase analysis and intensity-dependent TA measurements provide strong backing. Furthermore, we conducted temperature- dependent investigations, which when combined with the pump-dependent experiments, shed light on the degree of carrier-phonon coupling. We firmly believe that all this important information regarding phonon modes and how

they couple with the photogenerated carriers may be applied to enhance the performance of Cs₂SnI₆-based devices in near future. □ Unlike the preceding study that examined the phonon dynamics, the final project, which is also based on Cs₂SnI₆, focuses on investigation of its exciton dynamics. The positioning of the excitons in its Brillouin zone is first ascertained through the theoretical findings. Subsequent to these assignments, we deployed TA spectroscopy to examine the temporal evolution of these excitons and found the decay of the high energy exciton to be quite delayed. Surprisingly, the formation of high energy excitons is still observed even when the incoming photon energy is insufficient. The rationale for this result, we observed, is that the generation and decay processes of these excitons are entangled and are mediated by intervalley scattering mechanisms. In conclusion, our findings suggest that Cs₂SnI₆ might be a promising candidate in hot carrier-based solar cell systems that need delayed decay of high energy excitons.

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