Role of Lead Vacancies for Optoelectronic Properties of Lead-Halide Perovskites

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Methylammonium lead iodide perovskite materials have been shown to be efficient in photovoltaic devices. The current fabrication process has not been perfected, leaving defects such as site vacancies, which can trap charge and have a detrimental effect on the collection of photogenerated charge carriers. Here, the focus is placed on the effect a Pb site vacancy has on the charge carrier dynamics following photoexcitation. Excited state electronic structures are often found in open shell configurations with a single unpaired electron in the conduction band. To accurately describe unpaired electrons, spin-polarized calculations are performed on both neutral and charged systems. This work presents spin-polarized ground state electronic structures, non-radiative rates of charge carrier relaxation, and introduces an extension to a novel procedure to compute photoluminescence spectra for open shell models.[1] Electronic structure calculations are done in VASP with the PBE functional and plane wave basis set and the charge carrier dynamics are computed using Redfield theory within the reduced density matrix formalism. Early results show the vacancy of the Pb ion introducing a new energy state within the unblemished material band gap region. This additional unoccupied state is expected to increase the non-radiative relaxation lifetime of the excited electron, allowing for a longer lifetime of the charge carrier and increased opportunity for secondary relaxation mechanisms or collection to take place. The Pb vacancy presents an opportunity for polaron generation as the localization of charge due to atomic rearrangement carrier may be connected to directed orientation of the surrounding molecular dipoles. This type of change in molecular orientation can have direct effects into charge carrier motion, mobility, and collection in a photovoltaic device.

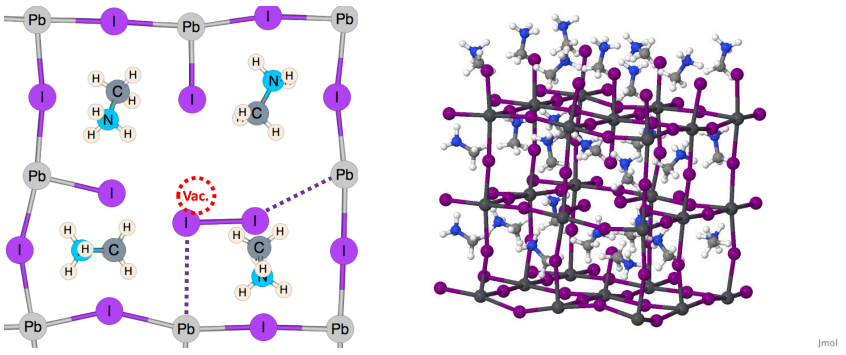

Figure 1. Model of 3x3x3 cubic MAPbI3 perovskite with central Pb-vacancy (Vac). Anionic configuration facilitates formation of quasistable I_2 molecules at the place of Pb vacancy.

1. Vogel, D. J.; Kilin, D. S., First-Principles Treatment of Photoluminescence in Semiconductors. *The Journal of Physical Chemistry C* **2015,** *119* (50), 27954-27964.