ATOMISTIC SIMULATIONS OF MIXED HALIDE PEROVKSITES: IS COMPOSITIONAL DISORDER DETRIMENTAL?

Claudio Quarti[1]

[1]*Laboratory for Chemistry of Novel Materials, Materials Research Institute, University of Mons, Belgium*
claudio.quarti@umons.ac.be

By combining impressive electronic properties together with wide compositional “tailorability”, solution-processed halide perovskites are emerging as ideal candidates for opto-electronics.[1] The possibility of tuning their chemical compositions via halide mixing, in particular, paves the way for band gap modulation within the full visible spectrum,[2] which is a key requirement for the development of color-tunable LEDs,[3] and wide band gap components in silicon-based PV cells.[4] On the other hand, such compositional inhomogeneity represents an intrinsic source of disorder in these semiconductors, hence leading to the fundamental question *“whether such disorder may negatively influence the intrinsic electronic properties of halide perovskites, and to which extent?”* This question was early investigated via optical spectroscopy, namely using Urbach tail and photoluminescence linewidth analyses.[5] Still, complex phenomena as light-triggered ion diffusion and formation of halide segregated domains hinders the rationalization of the experimental findings, hence calling for complementary theoretical simulations.

We hence performed parameter-free, periodic Density Functional Theory (DFT) simulations of mixed halide perovskite atomistic models. Cutting edge hybrid DFT calculations including spin-orbit-coupling point out that halide substitution does not lead to formation of intragap trap states, both in the dilute limit and in the case of homogeneously distributed iodine/bromine ions. Only in the case of halide segregation, the valence band maximum localizes in the iodine-rich domain, the bromine-rich domain acting as a barrier to hole diffusion.[6] We also included thermal-driven vibrational motion, resorting to DFT-based molecular dynamics simulations.[7] This allows to grasp the influence on the electronic properties due to “static” compositional disorder from iodine/bromine mixing and “dynamic” structural disorder associated with phonons, at once. Band gap broadening resulting from real-time ion dynamics falls in reasonable agreement with linewidth from photoluminescence,[8] finite-temperature simulations showing very small inhomogeneous contribution to broadening, both for pure halide and homogeneously dispersed iodine/bromine compositions. The increased broadening in segregated phases due to enhanced electron-phonon scattering, potentially associated with charge carrier recombination, also parallels experimental finding and we relate it to increased inhomogeneous, static contribution. This peculiar behaviour is associate with lattice mismatch at the iodine-rich/bromine-rich interface. All in all, our theoretical analyses point out that halide mixing does not negatively influences the electronic properties of perovskite semiconductors, except in the case of halide segregation, where more complicated mechanisms appear.

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