

Ionic Diffusion in Lead-Halide Perovskites from First-Principles Calculations

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Solar cells based on lead-halide perovskites have been proven to be remarkably efficient in recent years. However, they exhibit hysteresis in the current-voltage curves, and their stability properties, especially in the presence of water, are problematic. Furthermore, several recent studies emphasized the possibility of structural rearrangements under light. These issues are possibly related to defect migration phenomena occurring in the bulk perovskite material.

Here, we will present our recent first-principles results on defect diffusion and structural migration phenomena in hybrid and all-inorganic lead-halide crystals.[1,2] Specifically, our calculations are based on density functional theory and nudged-elastic band methods to sample structural trajectories and optimize minimum energy pathways of important intrinsic and extrinsic defect species.

First, the diffusion of hydrogen defects will be discussed,[1] which are known to be very important for many types of semiconductors, ranging from prototypical inorganic materials such as ZnO to organic ones and also oxide perovskites. We find that interstitial proton defects exhibit small activation energies for migration in MAPbI₃, and thus are likely mobile at room temperature. One key aspect in the migration mechanism is the mechanical flexibility of lead-halide crystals, which we find supports proton diffusion. We furthermore show that differently charged defects occupy different sites in the MAPbI₃ crystal, which allows for an ionization-enhanced defect migration following the Bourgoin-Corbett mechanism.

Second, our recent results on chlorine dopants in the all-inorganic perovskite CsPbI₃ will be presented.[2] Here, we found that interstitial Cl in a majority CsPbI₃ environment is also a fast moving defect species. Furthermore, at room temperature an anion exchange-reaction between an interstitial Cl and an iodide part of the perovskite lattice can occur, showing that Cl can be easily integrated into the CsPbI₃ host. The importance of Cl inclusion for the electronic and structural properties of lead-halide perovskites will then be discussed.

References

- [1] David A. Egger, Leeor Kronik, Andrew M. Rappe, *Angew. Chem. Int. Ed.*, 54, 12437–12441 (2015).
- [1] Subham Dastidar, David A. Egger, Liang Z. Tan, Samuel B. Cromer, Andrew D. Dillon, Shi Liu, Leeor Kronik, Andrew M. Rappe, Aaron T. Fafarman, *in preparation*.