DFT Analysis of the Relative Stability of Lithium Halide Crystal Structures

Hayden O. Scheiber and Grenfell N. Patey

Chemistry Department, University of British Columbia, BC, Email: scheiber@chem.ubc.ca

All lithium halides exist in the rocksalt crystal structure under ambient conditions. In contrast, common lithium halide classical force fields more often predict wurtzite as the stable structure. This failure of classical models severely limits their range of application in molecular simulations of crystal nucleation and growth. Employing high accuracy density functional theory (DFT) together with classical models, we examine the relative stability of seven candidate crystal structures for lithium halides. We give a detailed examination of the influence of DFT inputs, including the exchange-correlation functional, basis set, and dispersion correction. We show that a high-accuracy basis set, along with an accurate description of dispersion, are necessary to ensure prediction of the correct rocksalt structure, with lattice energies in good agreement with experiment. We also find excellent agreement between DFT-calculated rocksalt lattice parameters and experiment when using the TMTPSS-rVV10 exchange-correlation functional and a nearly complete basis set. Detailed analysis shows that dispersion interactions play a key role in the stability of rocksalt over closely competing structures. Hartree-Fock calculations, where dispersion interactions are absent, predict the rocksalt structure only for LiF, while LiCl, LiBr, and LiI are more stable as wurtzite crystals, consistent with radius ratio rules. Anion-anion second shell dispersion interactions overcome the radius ratio rules to tip the structural balance to rocksalt. We show that classical models can be made qualitatively correct in their structural predictions by simply scaling up the pairwise additive dispersion terms, indicating a pathway towards better lithium halide force fields.