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Tolerance factors for organic-inorganic perovskites: Applicability only for high temperature phases

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A valuable geometrical concept for the prediction of stable perovskite compounds was found in the Goldschmidt Tolerance Factor (TF), which relates the ionic radii of the constituents in a semi-empirical manner ($TF = \gamma_A + \gamma_X / \sqrt{2}(\gamma_B + \gamma_X)$). However, due to the chemically soft nature of the halide anions in the organic-inorganic perovskites and the accompanied higher co-valency, it is necessary to consider the ability of coordinating the different individual metal ions. This is accomplished by introducing the octahedral factor ($\mu = \gamma_B / \gamma_X$) allowing together with the TF, a 2D mapping of ABX_3 stability criteria. The main difficulty lies in the determination of an effective ionic radius for the organic cation, since van-der-Waals interactions and hydrogen bonding give rise to alternated steric demands and varying bond lengths with respect to the inorganic framework. Affirmative, theoretical and experimental values for radii of commonly used cations methyl ammonium (MA^+) and formamidinium (FA^+), range with a quite large variation from 1.8 to 2.7 Å for MA^+ and from 2.2 to 2.79 Å for FA^+. In the present work, steric sizes of molecular mono-ammonium cations were calculated by concerning free rotation of the electron density around the center of mass of the molecule. Thereby, structural optimizations were intensively investigated regarding the level of theory and basis sets. A thorough literature study about existing hybrid perovskite compounds revealed a high success rate of predicted stability criteria and 3D phase formation. Furthermore, a case study including the smaller hydroxyl ammonium (HA^+) replacing MA^+, confirmed the key role of the cationic size on the structural stability and revealed negligible energy barriers associated with preferred molecular orientations in the cuboctahedron. The newly developed computational approach is well suited for high temperature phases, since it considers thermally enabled movements of the central cation and the associated averaging of inorganic deformations.
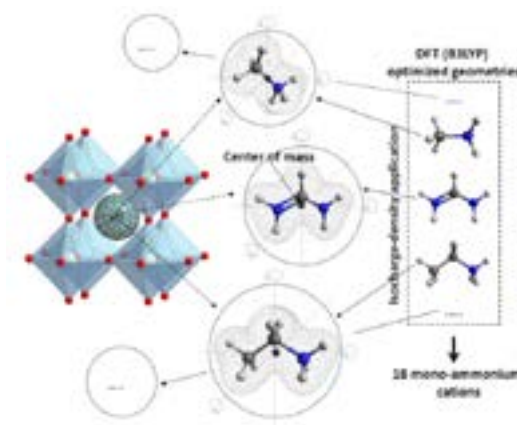

Figure 1: Scheme of determining the effective ionic radii of molecular cations for the calculation of tolerance factors in ABX_3 perovskites.

Biography

Markus Becker has his expertise in the development and improvement of sequentially deposited planar perovskite solar cells. One of his main focuses lies on the computational investigation of alternative absorber materials. Therefore, a contextual model has been built which allows the prescreening of possible three-dimensional perovskite phases. Combined with more elaborate DFT protocols, new combinations can be investigated considering the thermally enabled movement of the central cation. He has built this model after years of experience in research at University of Oldenburg, Germany.

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