Explicit Molecular Ordering and Structure–Property Relationships in Lead-Free Organic–Inorganic Hybrid Ge- and Sn-Based Halide Perovskites

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Abstract:

Lead-free hybrid halide perovskites based on Sn and Ge have emerged as promising alternatives to Pb-based compounds for photovoltaic applications. Their structural and electronic properties are strongly influenced by the coupling between the inorganic framework and the orientational ordering of the organic molecular cations. Although extensive first-principles studies have been reported for hybrid halide perovskites, most theoretical models simplify the organic cations by replacing them with effective spherical ions or by constraining their orientations within small unit cells. Such approximations neglect long-range orientational correlations and their coupling to the inorganic framework, limiting the description of cooperative structural distortions and their impact on the electronic properties.

In this work, we address these limitations by performing density functional theory (DFT) calculations with DFT-1/2 quasiparticle corrections, including relativistic effects, for $CH_3NH_3GeI_3$ ($MAGeI_3$), $CH_3NH_3SnI_3$ ($MASnI_3$), $CH(NH_2)_2GeI_3$ ($FAGeI_3$), and $CH(NH_2)_2SnI_3$ ($FASnI_3$) in cubic and orthorhombic phases. Explicit atomistic models of the methylammonium (MA) and formamidinium (FA) molecular cations were employed, and large supercells were used to investigate cooperative orientational ordering beyond the unit-cell approximation. The DFT-1/2 approach provides quasiparticle-level

band-gap corrections at a computational cost comparable to that of conventional DFT, making it suitable for the large-scale calculations performed in this work.

The calculations reveal that the organic molecular geometry remains essentially unchanged regardless of composition or crystal phase, whereas the inorganic metal–iodide framework accommodates the structural distortions governing the electronic properties. Structural relaxations further show that the ideal cubic phases spontaneously evolve into pseudo-cubic structures as a result of the symmetry-breaking induced by the explicit organic molecular cations within the unit cell. Substituting Ge with Sn systematically expands the lattice, reduces the band gap, and yields lighter carrier effective masses owing to the stronger Sn–I orbital hybridization. Orthorhombic phases are energetically favored for FA-based compounds, while MA-based systems exhibit much smaller energy differences between competing phases, indicating greater structural flexibility. Despite these structural variations, all investigated compounds retain a direct band gap, with its magnitude and the carrier effective masses being strongly controlled by the crystal symmetry and the choice of the group-IV metal.

These results demonstrate that the dominant structural response occurs in the inorganic framework, whereas explicit treatment of molecular orientations is essential to capture long-range structural correlations governing stability and electronic transport in lead-free hybrid perovskites.