Atomic and electronic structure of cesium lead triiodide surfaces

Cesium lead triiodide ($CsPbI_3$) has recently emerged as a promising optoelectronic material with enhanced stability for application in solar cell techniques compared to hybrid organic-inorganic perovskite materials. To harness the full potential of $CsPbI_3$ as a photovoltaic material, there is the need to understand its surfaces and reconstruction mechanisms. So far the surfaces and interfaces of $CsPbI_3$ have not been fully understood. Using first-principles methods and surface phase diagram (SPD) analysis, we study surfaces and electronic properties of the cubic (α) and orthorhombic (γ) phases of $CsPbI_3$. We compare CsI - and PbI_2-terminated surfaces along the (001) plane. We find that CsI-termination is more stable than PbI_2-termination. For the CsI-terminated surface, we then compute and analyse the surface phase diagram. We observe that surfaces with added or removed units of nonpolar CsI and PbI_2 are most stable. The corresponding band structures reveal that the α phase exhibits surface states that derive from the conduction band. The surface reconstructions do not introduce new states in the band gap of $CsPbI_3$, but for the α phase we find additional surface states at the conduction band edge.