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Hexagonal Stacking Faults Act as Hole-Blocking Layers in Lead Halide Perovskites

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ABSTRACT: **The transformation between black (corner sharing) and yellow (face sharing) polytypes of lead halide perovskites is a major performance bottleneck. We investigate phase intermixing through the simulation of stacking faults (nanodomains) that reveal a small thermodynamic cost but large electronic consequences in $CsPbI_3$.**

The close competition between cubic-close packing (ABC) and hexagonal-close packing (AB) of elemental solids extends to crystals containing more than one element. In semiconductor physics, the cubic zincblende and hexagonal wurtzite polytypes both play important roles, and this extends to ternary and quaternary compounds.[1] Because of the small energy differences involved, stacking faults often emerge (e.g., AB sequences in an ABC structure) and can be found in thin-film photovoltaics such as CdTe.[2]

In metal halide perovskites, polytypes also play a key role as evidenced by the close competition between black (3C) and yellow (2H) phases for many compositions.[3,4] One distinction is that the ions in both zincblende and wurtzite maintain roughly tetrahedral coordination, while in perovskites the change in stacking sequence is associated with a transition from corner-sharing to face-sharing octahedral networks as illustrated in Figure 1. It has been established that the nanostructure of halide perovskites is nuanced with reports of local symmetry breaking, strain gradients, twin boundaries, and phase coexistence.[5,6]

We consider $CsPbI_3$ in four structures. Ramsdell notation (e.g., 11H) becomes ambiguous for complex stacking sequences, so we instead describe them according to whether each halide layer is corner or face-sharing (e.g., 3*c*8*h*) as illustrated in Figure 1. Each model was optimized with density functional theory (DFT/PBEsol)[7,8] including scalar relativistic effects using the technical setup reported elsewhere.[9] The spread in formation enthalpies is small (<20 meV/atom) and comparable to thermal energy at room temperature. The 2H structure is most stable for $CsPbI_3$ in our athermal calculations, consistent with other reports.[10,11] Taking into account the revised ionic radii,[12] the Goldschmidt tolerance factor of this iodide (0.89) is less than ideal.

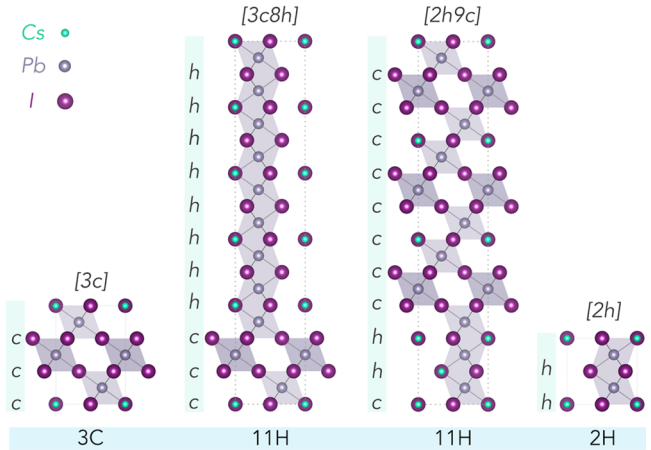

Figure 1. Illustration of four polytypes for $CsPbI_3$. The traditional cubic perovskite (3C) consists of corner-sharing PbI_6 octahedra. In contrast, a face-sharing octahedral network is formed in the hexagonal (2H) structure. Two 11H polytypes are shown, which can be distinguished according to the iodine in each layer being corner-sharing (*c*) or face-sharing (*h*). Note that the stacking axis corresponds to the ⟨111⟩ direction for a cubic perovskite unit cell.

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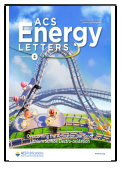

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Table 1. Properties of $CsPbI_3$ with Corner-Sharing, Face-Sharing, and Mixed Stacking Sequences[a]

stacking	a (Å)	c (Å)	ΔH_f	SFE	VBO	CBO	E_g (I)
2H (2h)	8.42	6.57	0				2.56 (1.86)
11H (3c8h)	8.49	41.98	6	0.11	−0.12	−0.07	2.10 (1.81)
11H (2h9c)	8.72	40.96	15	0.07	−0.26	0.00	1.44
3C (3c)	8.83	10.81	18				1.18

[a]The formation enthalpy (ΔH_f) is given with respect to the lowest-energy polymorph (meV/atom). The stacking fault energy (SFE) is given in eV/nm^2. The valence and conduction band offsets (VBO/CBO) are given in eV. E_g refers to the direct (and indirect, I) band gap in eV. Note that band gaps are underestimated at this level of theory (DFT/PBEsol).

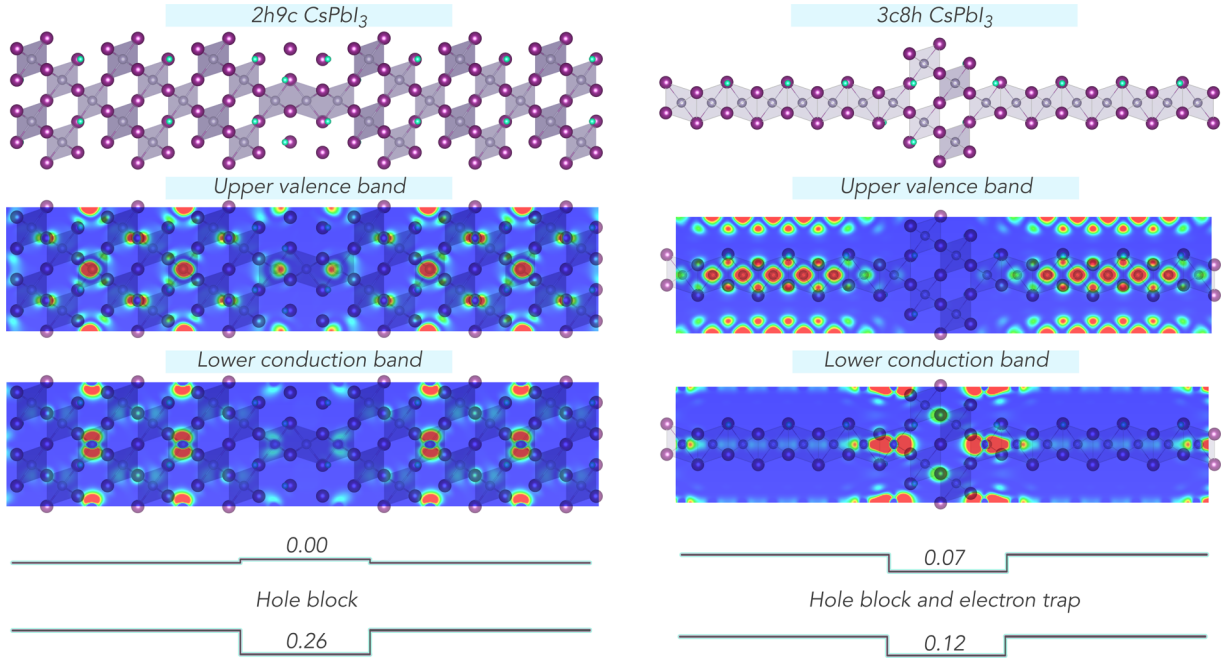

Figure 2. Electron density distribution associated with the highest occupied and lowest unoccupied crystal orbitals for stacking faults in $CsPbI_3$. The electron density is plotted through a (100) slice containing Pb and I atoms from blue (zero density) to red (high density).

We define an effective stacking fault energy (SFE) that describes the miscibility of corner and face-sharing regions as

$$\mathrm{SFE}_{NcMh} = \frac{1}{A}\left(E_{NcMh} - \frac{N}{3}E_{3c} - \frac{M}{2}E_{2h}\right) \quad (1)$$

E represents the DFT total energy, and N and M are the number of corner-sharing and face-sharing layers, respectively. The corresponding values are listed in Table 1. The cubic fault in a hexagonal structure has a cost of 0.11 eV/nm^2, which is lower than that of tetrahedral semiconductors.[2] The hexagonal fault in cubic $CsPbI_3$ results in an even smaller SFE. This result is a consequence of the enhanced stability of 2H over 3C for $CsPbI_3$ at 0 K. The calculations confirm that stacking faults in halide perovskites have a small thermodynamic cost and are therefore likely to form.

To assess the electronic consequences, we have analyzed the band structure and alignments. The 2H sequence results in a larger indirect band gap relative to 3C, as expected. The two mixed models show intermediate behavior with a larger indirect band gap (3c8h) and a smaller direct band gap (2h9c). The band offsets were probed through analysis of the band-edge electron density, electrostatic potential, and core-level distributions. These unanimously confirm a preference for strong hole blocking by the stacking faults (Figure 2). The lower conduction band is always formed in the corner-sharing regions; however, the upper valence band can be formed in the corner-sharing (for 2h9c) or face-sharing (for 3c8h) regions.

For the c region in the h structure, there is a staggered type-II band offset that results in selective trapping of electrons with a 0.07 eV potential well. For the h region in the c structure, the valence band exhibits a much larger shift (0.26 eV) compared to the conduction band (0.001 eV), which would result in a strong hole-blocking effect but no electron trapping.

Significant polarization is observed at the boundaries of the polytype regions, as evidenced by the distorted Pb 6s (valence band) and Pb 6p (conduction band) charge density, as well as the displacements of Cs atoms, in Figure 2. Such interface dipoles could be large enough to change the nature of the band offset type and behavior, depending on the size and orientation of the polytype arrangement on each side of the junction. We note that the $P6_3mc$ space group of 2H is noncentrosymmetric and piezoelectric; the properties of such junctions will be sensitive to crystal strain.

Our central conclusion is that although corner-sharing and face-centered halide perovskite polytypes are well studied, they represent two extremes. A spectrum of structures exist in between them with more complex stacking sequences, as evidenced by recent reports.[13] We have shown that hexagonal inclusions can readily form in halide perovskite crystals and their primary effect will be to suppress hole transport across grains. Crystal engineering to obtain mixtures of corner- and face-

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sharing octahedral networks opened an avenue to obtain new functionality in oxide perovskites.[14] Building on progress in high-resolution microscopy of halide perovskites,[6,15] deeper experimental and theoretical investigations into polytype stability and stacking fault behavior, including the role of chemical composition, is warranted.

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Notes

The authors declare no competing financial interest.

Structural models were generated for the two stacking faults starting from the crystal structure of pristine cubic $CsPbI_3$. The structure models and the code used to generate them are available in an online repository at http://doi.org/10.5281/zenodo.3878743.

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