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Stabilization of Black FAPbI$_3$ Perovskite by Interaction with the Surface of the Polymorphic Phase α-PbO

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Abstract: The black phase of formamidinium lead iodide, FAPbI$_3$, is optically active and promising for optoelectronics applications. However, it is difficult to synthesize and stabilize at room temperature since it thermodynamically tends toward the photoinactive yellow phase. Based on density functional theory computations, the potential of PbO semiconductor substrates to stabilize the black phase of FAPbI$_3$ perovskite is investigated and shown that, interestingly, it can be effectively stabilized over the yellow phase at room temperature when deposited on the polymorphic phase α-PbO.

1. Introduction

Current halide perovskite-based optoelectronic devices are affordable and efficient, with high photoconversion efficiencies especially in the case of solar cells.[1] In the vast family of halide perovskite materials, only those containing methylammonium (MA$^+$), formamidinium (FA$^+$), and Cs$^+$ cations result in 3D perovskites with charge transport properties suitable for high performance photovoltaics. Furthermore, perovskites with FA$^+$ cation show the narrowest band bap, close to the ideal one marked by the Schockley–Queisser limit, as well as high stability against heat. For these reasons, FAPbI$_3$ is a perovskite compound under intense research nowadays.[2] It crystallizes in two phases, black (perovskite) and yellow (hexagonal and non-perovskite); the black one refers, indeed, to cubic (α) and tetragonal (β and γ) phases.[3] At room temperature, the stable phase is the yellow phase (δ), of null interest in optoelectronics because of a large band gap of 2.43 eV.[4,5] It turns out that black FAPbI$_3$[6–10] is photoactive yet stable only beyond 165 °C. One strategy to produce black FAPbI$_3$ at room temperature consists in synthesizing at high temperatures and cooling down afterwards. However, the resulting metastable crystals rapidly evolve towards the yellow phase.[11] Another strategy to stabilize black FAPbI$_3$ at room

temperature consists in replacing the FA$^+$ cations and/or the I$^-$ anions by other species or moieties.[12–16] This strategy yields, unfortunately, band gaps which are far from optimal.[17,18] Including PbS quantum dots[3] in a FAPbI$_3$ matrix has proven an effective strategy to stabilize black FAPbI$_3$ while preserving its narrow band gap. Indeed, FAPbI$_3$-based perovskite solar cells fabricated with embedded PbS quantum dots exhibit superior operational performance and longevity than those fabricated with metastable FAPbI$_3$. The superior longevity is related to the presence of PbOx products and Pb−O bonds in the FAPbI$_3$ nanofilms, which block the phase transformation from black to yellow.[19]

Following the promising results previously obtained with PbS quantum dots[3,20] and the relevant role of these Pb−O bonds, in this work we investigate the potential use of PbO surfaces to stabilize the black phase of FAPbI$_3$ at room temperature. Lead oxide is a photoactive material with a broad spectrum of applications and two polymorphs, α and β.[21–25] The α-PbO is a red compound stable at room temperature known as litharge, with a band gap in the range of 1.9–2.2 eV. As for the β polymorph, it is a yellow material only stable at temperatures above 488 °C which is known as massicot, with a band gap of 2.7 eV. The crystallographic data of these two compounds are available from the ICSD database: α-PbO is tetragonal with unit cell (in Å) (a,b,c) = (4.06, 4.06, 5.30), and β-PbO is orthorhombic with unit cell (a,b,c) = (5.90, 5.49, 4.75).

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2. Computational Method

Computer calculations in this work were conducted with Quantum Espresso,[26] a density functional theory (DFT) code based on plane waves and pseudopotentials, which provides converged atomic structures and total energies at the ground state. In detail, we used a Monkhorst–Pack grid of k-points in the first Brillouin zone of the reciprocal space, pseudopotentials generated with the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBEsol[27]), spin orbit interactions, a threshold force of 5 meV Å^{-1} for the geometrical relaxations, and for 2D systems such as slabs, substrates, and heterojunctions,[28] dipole corrections and a void space of 12 Å between neighbor supercells.

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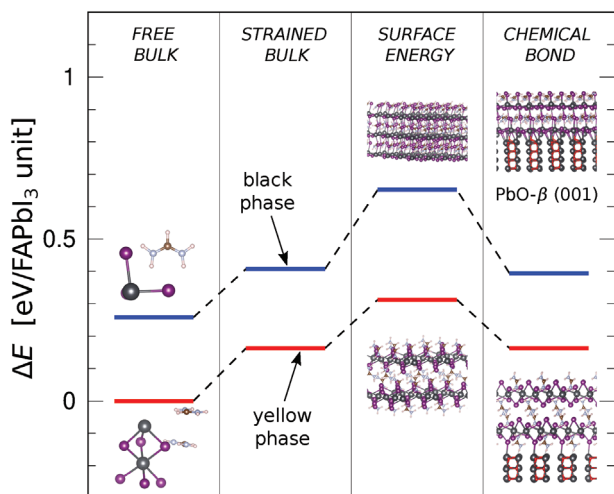Open Access

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Figure 1. DFT total energy per formula unit calculated for black and yellow FAPbI$_3$ materials in the free bulk, in a strained bulk, in a strained slab, and in a heterojunction formed by FAPbI$_3$ on β-PbO substrate with orientation (001).
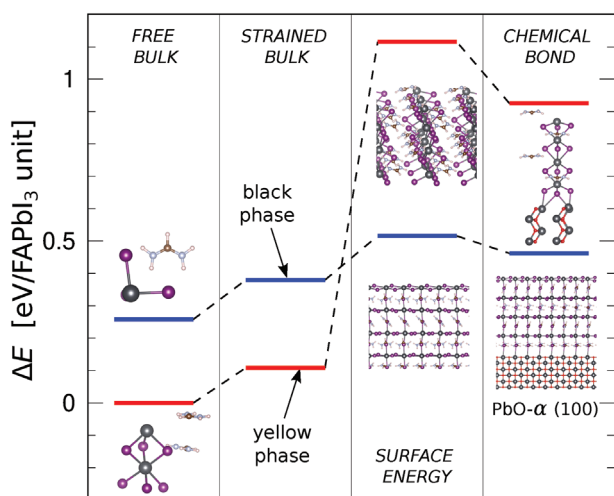

Figure 2. DFT total energy per formula unit calculated for black and yellow FAPbI$_3$ materials in the free bulk, in a strained bulk, in a strained slab, and in a heterojunction formed by FAPbI$_3$ on α-PbO substrate with orientation (100).

3. Results and Discussion

The stabilization of black FAPbI$_3$ by PbO substrates involves the following three actors: i) strain in the FAPbI$_3$ grown layer resulting from the mismach at the contact plane; ii) surface energy on the FAPbI$_3$ side; and iii) chemical interaction between the two materials. In order to establish reference energy levels, we first calculated bulk FAPbI$_3$ in both black (α, cubic) and yellow (δ, hexagonal) phases and obtained their respective total energy levels; they are plotted in panels labeled as "FREE BULK" in **Figures 1** and **2**. As expected, the DFT total energy of FAPbI$_3$ bulk in the black phase exceeds the one in the yellow phase by 0.26 eV per formula unit; this explains the thermodynamic trend of the black phase toward the more stable yellow phase.

To assess the effect of strain on FAPbI$_3$ deposited on PbO, we computed the same bulk FAPbI$_3$ unit cells, black and yellow, yet constrained to the dimensions of the PbO substrate. We assumed that most of the strain occurs on the FAPbI$_3$ side, due to the rigid (soft) bonds of PbO (FAPbI$_3$). The unit cells of FAPbI$_3$ were forced to match the surface PbO planes (100) for the α-PbO polymorph and (001) for the β-PbO polymorph. These surfaces were carefully chosen based on a small mismatch at the contact, which was checked by comparing interatomic distances and angles in the relaxed geometries of FAPbI$_3$–PbO heterojunctions, drawn in **Figure 3**, to the ones in the experimental cubic unit cell,[29] which are 6.36 Å and 90°, respectively. The resulting energy values, plotted in panels labeled as "STRAINED BULK" of Figures 1 and 2, show that strain destabilizes black and yellow phases in approximately the same amount, and that this effect is slightly more pronounced for FAPbI$_3$ constrained to the surface β-PbO (001) than subject to α-PbO (100).

Furthermore, to study the effect of surface formation and surface energies, strained slabs of about 2 nm created from the same strained bulk FAPbI$_3$ unit cells were computed, see panels labeled as "SURFACE ENERGY" in Figures 1 and 2. As expected, the presence of surfaces increases the energy per formula unit with respect to the strained bulk compounds black and yellow, by $\approx$1 eV indeed for a slab of yellow FAPbI$_3$ constrained to the dimensions of α-PbO (100).

The last factor to be considered was the chemical binding of FAPbI$_3$ to the PbO substrate. The interactions between both materials were studied upon heterostructures of FAPbI$_3$ grown on PbO, see Figure 3 and panels labeled as "CHEMICAL BOND" in Figures 1 and 2. In order to obtain the total energy per formula unit of FAPbI$_3$ in these heterostructures, we proceeded in three steps following ref. [3]. First, we computed the FAPbI$_3$–PbO heterojunction and its DFT total energy; second, we computed the PbO substrate and its total energy; and third, we subtracted both energy values and divided the subtraction by the number of formula units in the FAPbI$_3$ layer. Both FAPbI$_3$ possible terminations on the PbO substrate, namely I−FA−I and Pb−I−Pb, were considered and computed. On the α-PbO (100) substrate, the lowest energy and thus most stable termination is I-FA-I, with chemical bonds I(FAPbI$_3$)−Pb(surface) between both materials. On the β-PbO (001) substrate, the termination is Pb−I−Pb, with chemical bonds Pb−O and I−Pb. As expected, contact interactions produce a decrease of the total energy per formula unit, which we ascribe to covalent bond formation and electrostatic potential at the interface.

In brief, our DFT calculations show that, first, strain does not play a role in the stabilization of black FAPbI$_3$. Second, β-PbO substrates with orientation (001) do not stabilize black FAPbI$_3$. Surface energies and contact interactions cancel each other out for both FAPbI$_3$ phases black and yellow, in order that the yellow phase remains more stable than the black phase, see panel "CHEMICAL BOND" in Figure 1.

Third and last, the black phase of FAPbI$_3$ is less stable than the yellow phase when grown on β-PbO (001), yet more stable when grown on α-PbO (100), follow panels "CHEMICAL BOND". Surfaces play here a determinant role and contact interactions are secondary. Indeed, the surface energy of a slab of yellow FAPbI$_3$ constrained to the α-PbO (100) surface is significantly greater than the one of black FAPbI$_3$ on the same substrate, see panel

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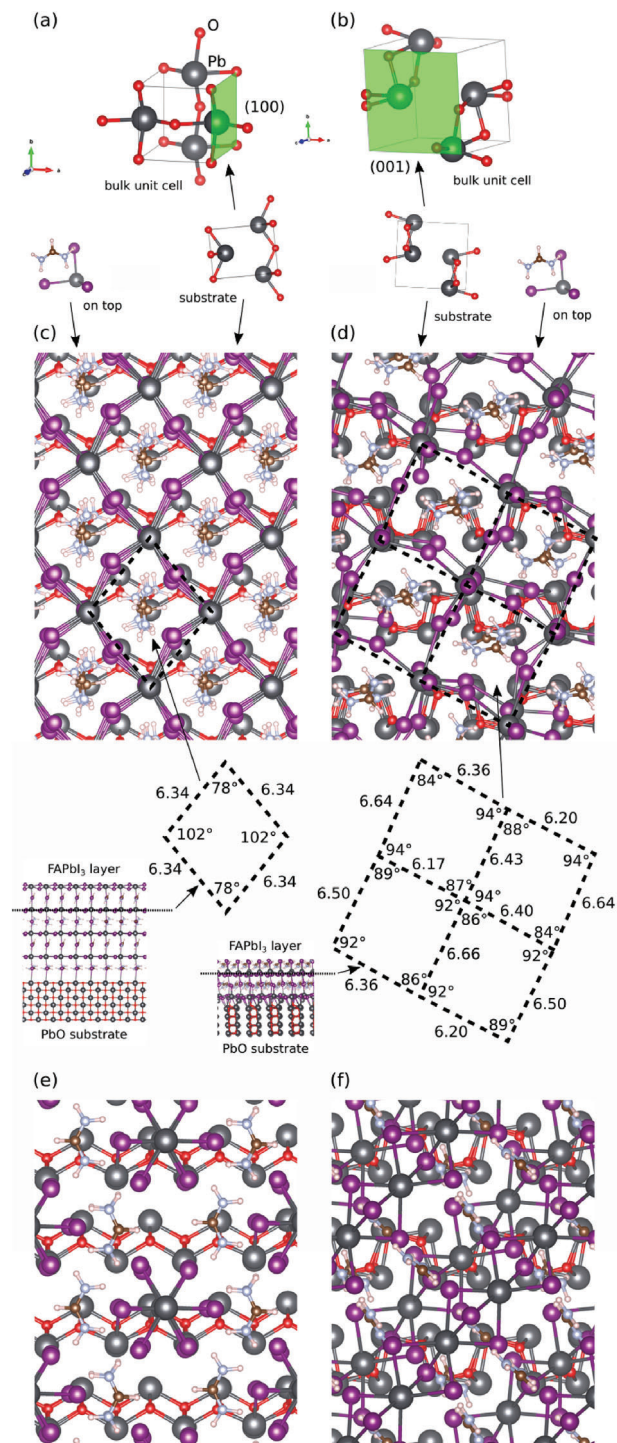Open Access

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Figure 3. Bulk polymorphs a) α-PbO and b) β-PbO with indication of crystalographic planes (100) and (001), respectively. Top views of heterojunctions of black FAPbI$_3$ perovskite deposited on a substrate of c) α-PbO with orientation (100) and d) β-PbO with orientation (001). Top views of heterojunctions of yellow FAPbI$_3$ deposited on a substrate of e) α-PbO (100) and f) β-PbO (001). We include dashed polygons with indication of Pb–Pb interatomic distances (in Å) and angles at the pointed planes.

"SURFACE ENERGY" in Figure 2. In comparison, the difference between surface energies for black and yellow FAPbI$_3$ slabs constrained to the β-PbO (001) substrate is small. We note that the calculated splitting of 0.47 eV obtained between black and yellow phases grown on α-PbO (100), see "CHEMICAL BOND" in Figure 2, is approximately half the value reported for FAPbI$_3$ on PbS.[3] Moreover, the PbS rock-salt structure leads to smaller distortions at the contact than PbO. Therefore, the stabilization of black FAPbI$_3$ by PbS surfaces turns out to be more robust than by PbO.

4. Conclusions

In summary, in this work we have computationally investigated, at the atomic scale, the use of PbO surfaces to stabilize the photoactive black phase of FAPbI$_3$ perovskite—which is only stable beyond 165 °C—at room temperature. We have considered the PbO polymorphic phases α and β, and studied three factors involved in the stabilization of black FAPbI$_3$ perovskite by PbO: strain in the FAPbI$_3$ layer, surface energies on the FAPbI$_3$ side, and contact FAPbI$_3$–PbO chemical interactions. Interestingly, only the α polymorph of PbO is useful to stabilize the black phase of FAPbI$_3$ at room temperature, in agreement with previous experiments.[19] Motivated by these results, we encourage chemists to employ, in addition to PbS nanoparticles,[3,20] α-PbO nanocrystals such as quantum dots and nanoplatelets to stabilize the black phase of FAPbI$_3$ in future synthesis experiments.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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