Layered structures of organic/inorganic hybrid halide perovskites

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Organic/inorganic hybrid halide perovskites, formed by substituting the cations A of ABX$_3$ halide perovskites with certain organic cations, may be used for solar thermoelectric applications. In this work, we systematically study three lead-free hybrid perovskites, i.e., methylammonium tin iodide CH$_3$NH$_3$SnI$_3$, ammonium tin iodide NH$_4$SnI$_3$, and formamidinium tin iodide H(C(NH$_2$)$_2$)SnI$_3$, by first-principles calculations. We find that in addition to the commonly known motif in which the corner-sharing SnI$_6$ octahedra form a three-dimensional network, these materials may also favor a new motif formed by alternating layers of the SnI$_6$ octahedra and the organic cations. These two motifs are nearly equal in free energy and are separated by low barriers. Interestingly, the layered structures feature many flat electronic bands near the band edges, potentially improving the thermoelectric performances. Calculations within a semiclassical model indicate that the layered structures may indeed feature high thermoelectric figure of merit $\varepsilon T$, thereby suggesting further investigations on this promising structural motif of the hybrid halide perovskites.

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I. INTRODUCTION

Ternary compounds with the ABX$_3$ cubic perovskite structure, or simply perovskites, host an enormous number of functionalities, including ferroelectricity, colossal magnetoresistance, and high thermopower. The interest on this family has further been fuelled by the development of organic/inorganic hybrid halide perovskites in which cations A are substituted by organic cations like methylammonium CH$_3$NH$_3$ and ammonium NH$_4$ and formamidinium H(C(NH$_2$)$_2$). These imply that the hybrid halide perovskites are efficient materials for solar thermoelectric applications (the conversion efficiency has recently exceeded 18%).

In the pretty simple cubic perovskite structure, cations A sit at the centers of the cages formed by a three-dimensional (3D) network of connected BX$_6$ octahedra. When the large, anisotropic and polar organic cations are introduced at these sites, this structure is appreciably altered, typically resulting two new major structural motifs (see Fig. 1 for an illustration). The first motif, characterized by strongly distorted 3D network of BX$_6$ octahedra, was examined in almost all the reported computational works, showing great promises of future applications. In the second motif, the network is completely broken along one dimension, forming alternating layers of connected BX$_6$ octahedra and the organic cations. Although this two-dimensional (2D) layered motif was experimentally suggested for a few hybrid perovskites, computational efforts devoted to it appear to be limited. In a work based on first-principles calculations, the experimentally resolved structure of C$_4$H$_9$NH$_3$PbI$_4$ was found to have a slightly wide band gap $E_g$ accompanied with flat electronic bands dispersion nearby. These characteristics were also suggested for several nearly-2D structures of CH$_3$NH$_3$PbX$_3$ (X = Br, Cl), signaled by the calculated long/short/short/long pattern of Pb-X axial distances. Different from the 2D structure observed for C$_4$H$_9$NH$_3$PbI$_4$, the structures predicted for CH$_3$NH$_3$PbX$_3$ actually exhibit the 3D motif with an exception of slightly longer Pb-X axial distances along a given direction.

In this contribution, we systematically study three organic/inorganic hybrid lead-free halide perovskites, namely methylammonium tin iodide CH$_3$NH$_3$SnI$_3$, ammonium tin iodide NH$_4$SnI$_3$, and formamidinium tin iodide H(C(NH$_2$)$_2$)SnI$_3$ with calculations at the level of density functional theory (DFT). We show that the low-energy structures of these hybrid perovskites exhibit either the 2D or the 3D motif. For each material, the lowest-energy 2D and 3D structures are energetically competing, separated by a low energy barrier, $\Delta E_{2D-3D} \approx 15 - 20$ meV/atom. Interestingly, the 2D structures are found to be characterized by many flat electronic bands. Calculations within the Kane single band model for CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and H(C(NH$_2$)$_2$)SnI$_3$ suggest that the layered structural motif may improve their thermoelectric performances.

II. COMPUTATIONAL METHODS

Our DFT calculations were performed using ABINIT package employing the norm-conserving Hartwigsen-Goedecker-Hutter pseudo potential. The DFT energies $E_{DFT}$ were calculated with a basis set of plane waves with kinetic energy up to 810 eV, using the Perdew-Burke-Ernzerhof exchange-correlation functional. The Brillouin zone was sampled by Monkhorst-Pack k-point
FIG. 1. (Color online) Lowest-energy structures of CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and HC(NH$_2$)$_2$SnI$_3$: the 3D structure on the left and the 2D structure on the right. Sn, I, C, N, and H atoms are shown in yellow, purple, brown, lavender, and pink colors, respectively.

Possible low-energy structures of the hybrid perovskites were predicted with the minima-hopping method. Starting from a given initial structure, the associated configurational space is explored by alternating molecular dynamics and local optimization runs. By employing the Bell-Evans-Polanyi principle and several feedback mechanisms, the exploration by this method strongly favors the lower-energy subspace but climbing over the energy barriers is also allowed when necessary. The efficiency of this method has been proved for various classes of materials, including organic and especially, a large number of organic/inorganic hybrid compounds.

III. LOW-ENERGY STRUCTURES

From the minima-hopping searches, low-energy structures of these hybrid perovskites were predicted to exhibit either the 3D motif or the 2D motif. The lowest-energy structures of these motifs are nearly equal in the DFT energy $E_{\text{DFT}}$. In case of NH$_4$SnI$_3$ and HC(NH$_2$)$_2$SnI$_3$, the 2D structures are lower than the 3D structures by 3–10 meV/atom while the 3D structure of CH$_3$NH$_3$SnI$_3$ is lower than the 2D structure of this compound by roughly 4 meV/atom. We then focus on six lowest-energy structures, one 2D and one 3D structure for each of the three materials (their crystallographic information is provided in the Supplemental Material. These structures are visualized in Fig. 1 showing that while in the 3D motif, the topology of the ideal cubic perovskite structure is preserved, layers of connected BX$_6$ octahedra are unambiguously formed and strongly

FIG. 2. (Color online) Simulated x-ray diffraction patterns of the structures examined for CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and HC(NH$_2$)$_2$SnI$_3$.

FIG. 3. (Color online) Calculated phonon densities of states of the thermodynamically most stable 2D and 3D structures predicted for CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and HC(NH$_2$)$_2$SnI$_3$. For convenience, imaginary phonon frequencies, if any, are shown as the negative values of their magnitudes.
shifted with respect to each other. The difference between the 2D structure and the 3D structure is revealed in Fig. 2 where the relevant x-ray diffraction patterns simulated at the Cu Kα wavelength $\lambda = 1.54\text{Å}$ using FULLPROF suite are shown. We note that the lowest-energy 3D structure of CH$_3$NH$_3$SnI$_3$ studied in this work is identical with that studied in previous works, e.g., in Ref. [24].

Calculated phonon frequency spectra are typically used for examining the dynamical stability of a theoretically predicted structure. For this purpose, we performed relevant phonon calculations utilizing the linear response method as implemented in the ABINIT package. The phonon densities of states of these structure are shown in Fig. 3, clearly demonstrating that the predicted structures are dynamically stable as no imaginary phonon mode was found in the Brillouin zone.

While $E_{\text{DFT}}$ is determined at 0K, the thermodynamic stability of these structures at finite temperatures $T$ may be accessed by examining the Helmholtz free energy. It is estimated as $F(T) = E_{\text{DFT}} + F_{\text{vib}}(T)$ where the vibrational contribution $F_{\text{vib}}(T)$ is calculated within the harmonic approximation as:

$$F_{\text{vib}}(T) = r k_B T \int_0^\infty d\omega g(\omega) \ln \left[ 2 \sinh \left( \frac{\hbar \omega}{2 k_B T} \right) \right]. \quad (1)$$

Here, $r$ is number of degrees of freedom in the unit cell, $k_B$ is the Boltzmann’s constant, $\hbar$ is the reduced Planck’s constant, and $g(\omega)$ is the normalized phonon density of states at frequency $\omega$. We show in Fig. 4 the free energies computed for the six examined structures, revealing that the 2D structures of NH$_4$SnI$_3$ and HC(NH$_2$)$_2$SnI$_3$ are thermodynamically more stable than the 3D structures at low temperatures but gradually become less stable at elevating temperatures. In case of CH$_3$NH$_3$SnI$_3$, the 3D structure is always favorable over the 2D structure within the temperature range examined. Overall, the energy differences between the 2D and 3D structures examined are at the same order with $k_B T$.

IV. ACTIVATION BARRIERS

Because the 2D and 3D structures of CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and HC(NH$_2$)$_2$SnI$_3$ are nearly equal in energy, it is interesting to examine the energy barriers between them. For this purpose, we employed the solid-state (climbing image) nudged elastic band method to explore the minimum energy pathways between the 3D and the 2D structures of the hybrid perovskites. The calculated results are shown in Fig. 5, demonstrating that for these materials, the 3D and 2D structures are separated by low energy barriers, falling between 15 – 20 meV/atom. The structural transition from a 3D to a 2D structure involves breaking long Sn-I “bonds” along the out-of-plane direction and rotating both the in-plane Sn-I bonds and the whole organic cations. At operating temperatures (room temperature and above), these barriers are comparable with $k_B T$. For more information, the predicted pathways are provided in the Supplemental Material.
V. THERMOELECTRIC FIGURE OF MERIT

Thermoelectric figure of merit \( zT \) is a dimensionless parameter quantifying the efficiency of a thermoelectric material. It is defined as \( zT = S^2 \sigma T / (\kappa_E + \kappa_L) \) where \( S \) is the Seebeck coefficient, \( \sigma \) is the electronic conductivity, and \( \kappa_E \) and \( \kappa_L \) are the electronic and the lattice thermal conductivities. Typically, materials with \( zT \geq 1 \) may be considered to be advantageous for solar thermoelectric applications. Notwithstanding great efforts given, boosting \( zT \) remains a big challenge because \( S \), \( \sigma \), and \( \kappa = \kappa_E + \kappa_L \) are strongly coupled via many parameters in complicated ways.\(^{20}^{21}\) Lying at the heart of the “band structure engineering” approach for tailoring \( zT \)^{22} Mahan-Sofo theory\(^{23}^{24}\) suggests that if a local increase of the electronic density of states \( \rho(E) \) (here \( E \) is the carrier energy), e.g., a doping level, can be introduced in the vicinity of the Fermi level \( E_F \), \( zT \) may be improved, as realized by doping PbTe with 2% of Ti.\(^{25}\) Likewise, materials with flat electronic bands residing next to \( E_F \) may also be interesting because the resulted humps of the electronic density of states \( \rho(E) \) may play the role of the resonant levels as suggested by Mahan and Sofo.\(^{26}\)

Motivated by this discussion, we computed the electronic bands of the examined structures at the PBE level of DFT and show the results in Fig. \[\text{Fig. 6.}\] Interestingly, while the 3D structures are characterized by high-curvature parabolic bands, the 2D structures feature many flat bands next to the conduction band minimum (CBM) and the valence band maximum (VBM) as previously addressed\(^{13}^{22}\) thereby leading to significant resonant levels near the band edges (see Fig. \[\text{Fig. 6.}\]). Compared to the 3D structures, \( E_g \) of the 2D structures is considerably higher while their CBM degeneracy is unambiguously lifted. These characteristics affect \( zT \) in a mixed way, i.e., the flat bands may help but the degeneracy lifting reduces \( \sigma \) and hence, is deleterious for \( zT \).

We then estimated the figure of merit \( zT \) of the examined structures. Within the semiclassical Kane single band model\(^{53}\) \( zT \) is approximated as\(^{25}^{26}\)

\[
zT = \frac{1^F_{0,1}}{2} \left( \frac{1^F_{0,1}}{0^F_{1,2}} - \xi \right)^2 \left\{ \frac{2^F_{1,2}}{0^F_{1,2}} - \left( \frac{1^F_{0,1}}{0^F_{1,2}} \right)^2 \right\} + B^{-1} (3^F_{0,1})^{-1},
\]

where \( \xi = u/k_B T \) (\( u \) is the chemical potential) and the integral \( n^{F_m} \) is defined as\(^{52}^{53}\)

\[
n^{F_m} = \int_0^\infty \left( -\frac{df}{d\zeta} \right) \zeta^\alpha (\xi + \alpha \zeta^2)^m [(1 + 2\alpha \zeta)^2 + 2]^{1/2} d\zeta.
\]

Here, \( \alpha = k_B T / E_g \), \( f(\zeta) \) is the Fermi-Dirac distribution with \( \zeta = E/k_B T \) is the carrier energy in units of \( k_B T \). The “thermoelectric quality factor” \( B \) appearing in Eq. \[\text{2.}\] is calculated via\(^{22}^{24}\)

\[
B = \frac{2k_B^2 h}{3\pi} \frac{KN_C}{m_1^2 \Xi^2 \kappa_L} T
\]

where \( K \) is the bulk modulus, \( N_C \) is the band degeneracy, and \( \Xi \) is the deformation potential describing the carrier scattering strength by acoustic phonons. The inertia effective mass \( m_1 \) is governed by the effective band mass of a single electron pocket along two directions \( m_\perp \) and \( m_\parallel \) as \( m_1 = 3 (2/m_\perp + 1/m_\parallel)^{-1} \). All of these parameters are derived from first principles. In particular, \( K \) was
We show in Fig. 7 the figure of merit $zT$ calculated at $T = 300$ K for the examined structures, assuming $κ_L = 1$ W/mK as explained and used elsewhere. Although $zT$ computed for the 2D and 3D structures are promising and clearly different, especially in the optimal carrier density, it appears that there is no systematical (monotonic) trend relating the structural motif with $zT$. In particular, the 3D structure of CH$_3$NH$_3$SnI$_3$ is better than the 2D structure in terms of $zT$ while for NH$_4$SnI$_3$, the 2D structure is advantageous. These motifs are comparable in case of HC(NH$_2$)$_2$SnI$_3$. Presumably, the interplay of a large number of parameters as indicated above is why such the trend is hidden. However, the fact that $zT$ is significantly improved in the 2D structure of NH$_4$SnI$_3$ suggests that a comprehensive investigation of the all the possible layered structures of organic/inorganic hybrid perovskites are worth and desirable.

**VI. SUMMARY**

In summary, we have systematically studied three organic/inorganic hybrid perovskites, namely CH$_3$NH$_3$SnI$_3$, NH$_4$SnI$_3$, and HC(NH$_2$)$_2$SnI$_3$, by first-principles calculations at the level of density functional theory. We find that in addition to the 3D network of corner-sharing BX$_6$ octahedra, the 2D motif formed by alternating layers of connected BX$_6$ octahedra and organic cations may also be favorable. While these two structural motifs are energetically competing, they are separated by low barriers ($\approx 15 – 20$ meV/atom). All of the 2D layered structures are characterized by very flat electronic bands near VBM and CBM, potentially leading to thermoelectric performances improvements. We then use the semiclassical Kane single band model to estimate relevant performances of these structures, e.g., the figure of merit $zT$. Although the layered motif does not always improve $zT$, the 2D structure of NH$_4$SnI$_3$ is clearly promising. Thus, the revealed flat electronic bands dispersion suggest that further explorations on the layered structures of all the possible hybrid halide perovskites are desirable.

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