Influences of the orientations of CH$_3$NH$_3$ molecules on physical properties of organo-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$

Juanli Zhao $^{a,1}$, Peiyi Wang $^{a,1}$, Yuchen Liu $^{a,1}$, Bin Liu $^{b,*}$, Haixuan Xu $^{b,*}$

$^a$ School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China
$^b$ Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA

1. Introduction

The solar energy is a promising sustainable source to support the growing energy demand. A great many of systems and techniques have been implemented to harvest solar energy [1,2]. Among solar-energy conversion devices, photovoltaic solar cells that convert the solar energy directly to electricity are growing rapidly [3]. Presently, the high PCE (power conversion efficiency) of over 20% together with good overall performances including appropriate band gap and absorption coefficient make the silicon-based solar cells (SBSC) account for around 90% of the commercial market share [3-7]. However, the high-energy consumption during their production processes and high manufacture costs have entangled further commercially researches, which propels the development of novel photovoltaic solar cell materials [8]. As a promising photovoltaic material, CH$_3$NH$_3$PbI$_3$ that owns a high PCE of 20.84% for its appropriate band gap, high absorption coefficient, long carrier life and moderate carrier mobility, has been intensively investigated [8-13]. Meanwhile, the fabrication of the organo-inorganic hybrid perovskite do not require high purity of starting materials or advanced fabrication techniques [14].

The organo-inorganic hybrid perovskite has a formula of AMX$_3$, where A is an organic cation (methylammonium CH$_3$NH$_3$ or form midine CH$_3$CH$_2$NH$_3$), M a metal cation (Pb$^{2+}$ or Sn$^{2+}$) and X a halide anion (I$^-$, Br$^-$ or Cl$^-$) [15,16]. As the temperature increasing, CH$_3$NH$_3$PbI$_3$ undergoes a continuous phase transition as orthorhombic(O) $\longrightarrow$ 163 K $\longrightarrow$ tetragonal(T) $\longrightarrow$ 327 K $\longrightarrow$ cubic(C) [17]. Meanwhile, the CH$_3$NH$_3$I$_3$ molecule have an arbitrary orientation and interact with inorganic cage PbI$_3$ frameworks, which further influence the electronic/optical properties of CH$_3$NH$_3$PbI$_3$ [11]. Wierzbowska et al. found that the arbitrary orientation of CH$_3$NH$_3$ molecules can result in band gap changes [18]. Järv et al. proposed that the orientation of CH$_3$NH$_3$ molecules of the tetragonal phase CH$_3$NH$_3$PbI$_3$ has a great influence on its charge mobility (in the range of 50–66 cm$^2$/V$^{-1}$s$^{-1}$) [19]. Moreover, it is also believed to contribute to the high PCE of CH$_3$NH$_3$PbI$_3$ [20]. However, the comprehensive

* Corresponding authors.

E-mail addresses: binliu@shu.edu.cn (B. Liu), xhx@utk.edu (H. Xu).

$^1$ These authors contributed equally to this work.

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understanding the intrinsic properties of CH$_3$NH$_3$PbI$_3$ hybrid perovskite and the influence of the CH$_3$NH$_3$ molecular distribution in cubic and tetragonal phases are still lack.

In this work, the CH$_3$NH$_3$PbI$_3$ perovskites in cubic, tetragonal and orthorhombic phases are studied using DFT calculations. The accuracy of different functionals is tested at first and then the influence of organic molecular orientation on the crystal structures, electronic structures, optical and mechanical properties of cubic and tetragonal phases CH$_3$NH$_3$PbI$_3$ perovskites are clarified. Moreover, the mechanical properties are also investigated as the elastic moduli reflect the response of the structures to the elastic strain and are helpful to study its strain, stress, fracture mechanics and deformation properties [21–23]. These results are expected to arouse the attention on the effect of CH$_3$NH$_3$ molecular orientations on the crystal properties and guide the future performance optimization of CH$_3$NH$_3$PbI$_3$ through its structural design.

2. Computational models and methods

VASP 5.4.4 code was used to perform the density functional theory (DFT) calculations [34]. The generalized gradient approximation (GGA) in the forms of PBE (Perdew-Burke-Ernzerhof) and PBEsol (PBE for solid) with and without van der Waals (vdW) interaction (in the form of DFT-D3) were adopted as the exchange-correlation functional [25–27]. The van der Waals interaction generally was important in organic-inorganic materials with weak interaction. Moreover, it is known that the calculated band gap values of crystal structures are affected by different exchange-correlation potentials. Thus, the band gaps were also calculated by mBJ (modified Becke-Johnson) [28–30], SCAN (strongly constrained and appropriately normed) [31] and HSE (the screened hybrid functional of Heyd, Scuseria, and Ernzerhof) [32] approximations for comparison. In the mBJ and HSE calculations, the exact form of spin orbit coupling (SOC) [33] was also tested. The electron configurations considered here were: 1s$^2$ for H, 2s$^2$2p$^2$ for C, 2s$^2$2p$^3$ for N, 5s$^2$5p$^5$ for I, and 6s$^2$6p$^2$ for Pb. The cutoff energy and the K-points in reciprocal space were 450 eV and 4 × 4 × 4, respectively. The convergence criterion for structural optimization was that the maximum force on atoms; the supercells of tetragonal and orthorhombic structures have 48 atoms; the supercell of cubic phase includes 96 atoms; the supercells of tetragonal and orthorhombic structures have 48 and 96 atoms.

For the optical properties of these materials, we determined the dielectric function, reflectivity coefficients and absorption coefficients.

The dielectric function is calculated by [34]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

where, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real part and imaginary part, respectively. Then, the obtained dielectric function is used to calculate the reflectivity $R(\omega)$ and absorption coefficient $\alpha(\omega)$ through:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$

$$\alpha(\omega) = \sqrt{2\omega}(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega))^{1/2}$$

The elastic constants ($c_{ij}$) are calculated through the strain-stress relationship $\sigma_i = c_{ij}\varepsilon_j$. For each strain pattern, four strain amplitudes up to 0.4% were calculated. The compliance tensor ($s_{ij}$) is the inverse matrix of the elastic constant tensor, as $c_{ij} = (s_{ij})^{-1}$. $B$ and $G$ represent bulk and shear moduli, respectively, and they were obtained by Voigt-Reuss-Hill schemes [35–37].

$$B_V = \frac{1}{9} (c_{11} + c_{22} + c_{33} + c_{12} + c_{13} + c_{23})$$

$$G_V = \frac{1}{15} (c_{11} + c_{22} + c_{33} - c_{12} + c_{13} - c_{23}) + \frac{1}{3} (c_{44} + c_{55} + c_{66})$$

$$B_R = \frac{1}{3} (s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{13} + s_{23}))$$

$$G_R = \frac{15}{4} (s_{11} + s_{22} + s_{33} - 4(s_{12} + s_{13} + s_{23}) + 3(s_{44} + s_{55} + s_{66}))$$

$$B_H = \frac{1}{2} (B_V + B_I)$$

$$G_H = \frac{1}{2} (G_V + G_I)$$

Then, Young’s modulus $E$ and Poisson’s ratio $\nu$ are obtained using $B_H$ and $G_H$ as:

$$E = \frac{9B_H G_H}{3B_H + G_H}$$

$$\nu = \frac{3B_H - 2G_H}{2(3B_H + G_H)}$$

In general, anisotropic Young’s modulus represents the stiffness difference of each direction [38]. It can be shown by the three-dimensional surface of the orientation dependent Young’s moduli. The anisotropic Young’s modulus of cubic, tetragonal and orthorhombic crystals in terms of spatial surface are expressed as following equations, respectively [39]:

$$E = \frac{1}{E} = s_{11} - 2(s_{12} - s_{13} - \frac{s_{44}}{2})(t_1^2 + t_2^2 + t_3^2)$$

for cubic:

$$E = \frac{1}{E} = s_{11} (t_1^2 + t_2^2 + t_3^2) + 2s_{12} (t_1^2 + t_2^2 + t_3^2) + 2s_{44} (t_1^2 + t_2^2 + t_3^2)$$

for tetragonal:

$$E = \frac{1}{E} = s_{11} (t_1^2 + t_2^2 + t_3^2) + 2s_{12} (t_1^2 + t_2^2 + t_3^2) + s_{44} (t_1^2 + t_2^2 + t_3^2) + s_{55} (t_1^2 + t_2^2 + t_3^2)$$

for orthorhombic:

$$E = \frac{1}{E} = s_{11} (t_1^2 + t_2^2 + t_3^2) + 2s_{12} (t_1^2 + t_2^2 + t_3^2) + 2s_{13} (t_1^2 + t_2^2 + t_3^2) + s_{44} (t_1^2 + t_2^2 + t_3^2) + s_{55} (t_1^2 + t_2^2 + t_3^2) + s_{66} (t_1^2 + t_2^2 + t_3^2)$$

where, $l_1$, $l_2$ and $l_3$ are the direction parameters to three principal axes. The values of $l_1$, $l_2$ and $l_3$ are calculated by:

$$l_1 = \sin \theta \cos \varphi$$

$$l_2 = \sin \theta \sin \varphi$$

$$l_3 = \cos \theta$$

where, $\theta$ and $\varphi$ are angles between the radial vectors and axes, respectively.

3. Results and discussion

3.1. Crystal structure

Previously, the orientation of the CH$_3$NH$_3$ molecule in CH$_3$NH$_3$PbI$_3$ was ignored. However, the C–N axes in the CH$_3$NH$_3$ molecules are arbitrarily oriented along the diagonal directions of a single cell [40], which are considered here in order to clarify the influence of the molecular configuration on electronic structures, mechanical and optical properties. In this work, two different mode configurations are investigated, one with all C–N axes along the unitary orientation and the other with arbitrary distributed C–N axis orientations. For the cubic phase CH$_3$NH$_3$PbI$_3$ that has the space group of Pm3m, the structure with
the unitary orientation is defined as CUO (cubic phase with the unitary orientation) and that with the arbitrary orientation is CAO (cubic with the arbitrary orientation), as shown in Fig. 1(a) and (b), respectively. The functional (PBE, PBE + vdW, PBEsol and PBEsol + vdW) dependent cohesive energies and lattice constants of those two structures are illustrated in Fig. 1(c), together with the experimental lattice constants for comparison. The CAO structure has lower cohesive energies than CUO structure, indicating that the cubic phase of CH₃NH₃PbI₃ tends to have the arbitrary CH₃NH₃ molecular orientations. The result is well consistent with previous literature that the C–N axe is arbitrarily oriented in cubic structures as a result of thermal fluctuations [41]. Furthermore, the calculated results of PBE + vdW (6.33 Å for CUO, 6.24 Å for CAO) reproduce the experimental lattice constant (6.33 Å) better than other functionals [42].

Being similar to the cubic phase, two tetragonal phase (I4/mcm) structures of CH₃NH₃PbI₃, i.e. TUO (tetragonal phase with the unitary orientation) structure and TAO (tetragonal phase with the arbitrary orientation) structure are constructed as shown in Fig. 2(a) and (b), respectively. Fig. 2(c) shows that the TUO and TAO structures have nearly the same cohesive energies, indicating their comparable stability. Furthermore, both PBE + vdW and PBEsol correctly reproduce the experimental lattice parameters of a and c [43]. However, the orthorhombic CH₃NH₃PbI₃ phase (Pnma) has only one possible configuration as shown in Fig. 3(a). Since the orientation of CH₃NH₃ molecule is not along the unitary direction, it is named as OAO (orthorhombic phase with the arbitrary orientation) in this paper. According to the summarized calculated and experimental lattice constants in Fig. 3(b), all calculated lattice constants from PBE + vdW, PBEsol and PBEsol + vdW well reproduce the experimental values. Considering all above results, the PBE + vdW is used in the following property calculations because of its relatively more accurate reproduction in lattice constants for all phases [42,44].

3.2. Mechanical property

The elastic constants of all CH₃NH₃PbI₃ phases studied in this work are listed in Table 1. The number of independent elastic constants is nine for orthorhombic, six for tetragonal and three for cubic phases, due to their symmetry. It is found that the tensile related elastic constants (c₁₁, c₁₂ and c₃₃) of all materials are higher than their shear ones (c₆₆, c₅₅ and c₀₀). Furthermore, they all satisfy the Born-Huang stability criteria as [45]:

for cubic crystals:
\[ c_{11} > 0, \ c_{44} > 0, \ c_{11}+c_{12} > 0, \ c_{11}+2c_{12} > 0; \]

for tetragonal crystals:
\[ c_{11} > 0, \ c_{44} > 0, \ c_{11}-c_{12} > 0, \ c_{11}+c_{12}> 0, \ c_{11}+c_{33}-2c_{12} > 0, \ 2(c_{11}+c_{12})+c_{33}+4c_{12} > 0; \]

for orthorhombic crystals:
\[ c_{11} > 0, \ c_{22} > 0, \ c_{33} > 0, \ c_{44} > 0, c_{55} > 0, \ c_{66} > 0, \ c_{11}+c_{22}-2c_{12} > 0, \ c_{22}+c_{33}-2c_{23} > 0, \ c_{11}+c_{22}+c_{33}+2(c_{12}+c_{32}+c_{23}) > 0. \]

The elastic moduli reflect the response of the structures to the elastic strain [22,23]. In experiments, the polycrystalline bulk modulus B, shear modulus G and Young’s modulus E are always measured. As shown in Table 2, the bulk moduli increase in the order of cubic < tetragonal < orthorhombic, but the values of shear moduli and Young’s moduli are close. Meanwhile, the orientation of the CH₃NH₃ molecule has less influence on the moduli of the materials. Furthermore, the ratio of G/B is a widely accepted criterion of the brittleness and/or quasi-ductility nature of a material. If G/B is lower than the boundary value of 0.571, the material is quasi-ductile; otherwise, the material is brittle. Here, the G/B values of all compounds are lower than 0.571, indicating the possible quasi-ductility of CH₃NH₃PbI₃ which support its application as the thin film absorber [23].

Fig. 4 shows the surface contours of the direction dependent Young’s moduli of the five compounds. As shown in Fig. 4(a) and (b), the shapes of the two cubic phases with high symmetry are like a dice with equal values along three axes. For the tetragonal phases (Fig. 4(c) and (d)), the Young’s moduli are isotropic in (001) plane but exhibit strong anisotropy along the z-axis. In the case of the orthorhombic phase (Fig. 4(e)) that has lower symmetry than others, it is concave on the (001) and (100) plane and convex on the (010) plane. In order to compare their anisotropy quantitatively, the anisotropy index \( A^U \) is used to evaluate the anisotropy of all structures [46]. The \( A^U \) that is calculated from the Bulk module \( B_H \) and shear module \( G_H \) is defined as:
\[
A^U = \frac{5G_H}{G_H^2 + B_H^2} - 6
\]

If the crystal is isotropic, the value of \( A^U \) will be zero. With the increase of \( A^U \), the anisotropy of the Young’s moduli grows. The calculated \( A^U \) is 1.513 for CUO, 1.046 for CAO, 2.116 for TUO, 1.045 for TAO and 1.321 for OAO, indicating that the anisotropy of Young’s moduli enhances in order of TAO < CAO < OAO < CUO < TUO.

3.3. Band gap and optical property

The calculated band gaps of all structures using PBE with the van der Waals interactions are shown in Fig. 5, together with the experimental values for comparison [17,47,48]. The obtained band gaps of CAO, CUO, TAO, TUO and OAO using PBE + vdW are 1.58 eV, 1.43 eV, 1.61 eV, 1.65 eV and 1.74 eV, respectively, being in well agreement with experimental values and better than the results in previous literature (1.50 eV for cubic phase, 1.65 eV for tetragonal phase, 1.80 eV for orthorhombic
For CAO and TAO structures, the calculated band gaps accurately reproduce the experimental results with the deviation less than 0.06 eV. At the same time, the deviation between the calculated values and the experimental results of the band gaps for other structures are less than 0.14 eV. The calculated band structures using PBE + vdW are all collected in Fig. S1 in Supplementary. In addition, the obtained band gaps of these five CH$_3$NH$_3$PbI$_3$ structures using the mBJ, SCAN and HSE, together with and without considering the SOC effect, are all summarized in Table S1 and Table S2 in Supplementary. Comparing to experimental values, the calculated band gaps of CH$_3$NH$_3$PbI$_3$ are overestimated using the mBJ and HSE approximations, while those are underestimated using the SCAN functional (Table S1). Further considering the SOC effect, both mBJ and HSE potentials underestimate the experimental values (Table S2). However, all the band gaps calculated using these functionals exhibit larger deviation from experiments than those of PBE + vdW. Therefore, the following optical properties are studied using PBE + vdW functional.

The optical properties are crucial for photoelectric materials and
Here, the dielectric function \( \varepsilon(\omega) \), the absorption coefficient, and reflectivity of the CH\(_3\)NH\(_3\)PbI\(_3\) with different symmetry and the various CH\(_3\)NH\(_3\) molecular orientations are studied in detail. Fig. 6 (a) exhibits the real \( \varepsilon_1(\omega) \) and imaginary \( \varepsilon_2(\omega) \) parts of the dielectric functions in the range of 0 eV–5.2 eV for the studied five perovskite compounds. Due to the large band gap, the peak intensity for both real and imaginary parts of TAO, TUO and OAO structures are higher than that of CAO and CUO. At the same time, the positions (eV) of three dielectric peaks locating at the energy levels between 0 eV and 5.2 eV are collected in Fig. 6 (b). The energy levels of both the peaks of the real \( \varepsilon_1(\omega) \) and imaginary \( \varepsilon_2(\omega) \) parts are arranged in order of cubic > tetragonal ≈ orthorhombic. In addition, the orientation of the CH\(_3\)NH\(_3\) molecule also has a slightly influence on the dielectric functions. For the real part, the three peaks of the TRO structure and the third peak of the CAO structure move to higher energy levels comparing to the TUO and CUO structures, respectively; while the first and second peaks of the CAO structure move to the opposite direction. Similarly, in the case of the imaginary part, the two peaks of the TAO structure and the second peak of the CAO structure move to higher energy levels comparing to TUO and CUO structures, respectively; while the first peak of the CAO structure moves to the opposite direction.

The dielectric function directly affects the absorption coefficient and reflectivity. Figs. 7 (a) and 8 (a) illustrate the absorption spectra and reflectivity spectra of five CH\(_3\)NH\(_3\)PbI\(_3\) structures, respectively. It is found that both positions and intensities of the peaks in the absorption coefficient and reflectivity spectra are consistent with the imaginary part of the dielectric function. In terms of the peak intensity, the smaller the reflection peak is, the larger the absorption peak is. At the same time, we collect the peak positions of the absorption coefficient and reflectivity spectra in Figs. 7 (b) and 8 (b), respectively. The energy levels of the peaks for the absorption coefficient and the reflectivity are both in order of cubic > tetragonal ≈ orthorhombic. Furthermore, for the absorption coefficient, the three peaks of CAO structure move to lower energy levels comparing to those of CUO. Likewise, the first peak of TUO structure is in lower energy ranges than TAO; while the first peak of OAO structure moves towards the opposite direction. In the case of the reflectivity, the second peak of CAO structure and the first peak of TAO structure move to higher energy levels comparing to those of CUO and TUO, while the first and the third peaks of CAO structure, and the second and third peaks of TAO structure do the opposite direction movement. Lastly, the absorption edge that is calculated from the first peak of the absorption coefficient, is in the order of CUO (2.86) > CAO (2.76) > OAO (2.29) > TAO (2.24) > TUO (2.21). Therefore, it is naturally concluded that the orientation of the CH\(_3\)NH\(_3\) molecule does influence the absorption coefficient and reflectivity.

Moreover, the solid solution and/or doping have been accepted as effective strategies for the structure and performance modification of organo-inorganic hybrid perovskites [50,51]. For examples, Li et al.
[52] found that doping 1% CH$_3$SH$_2$ into CH$_3$NH$_3$PbI$_3$ can enhance the device performance by tuning the band gap and improving the PCE. It is found that doping Sn$^{2+}$, Sr$^{2+}$, Cd$^{2+}$ and Ca$^{2+}$ into the Pb$^{2+}$ position can effectively modify the band gap. The stronger the interaction between the metal dopant and iodine is, the smaller the band gap will be [53]. The CH$_3$NH$_3$PbI$_3$ doped with Al$_2$O$_3$ exhibits improved stability in damp [54]. Based on our results, it is believed that the dopants change the local environment (i.e., CH$_3$NH$_3$ orientations), which will affect the
In summary, the structural stability, electronic structures, mechanical and optical properties of CH$_3$NH$_3$PbI$_3$ in different phases are systematically investigated, in which the influence of the CH$_3$NH$_3$ molecular distribution in cubic and tetragonal phases is considered. We found that the CAO structure is more stable than CUO for the cubic phase, while the stability of TAO and TUO structures are comparable as revealed. At the same time, these materials all show anisotropic mechanical properties. Their anisotropy increases in order of TAO < CAO < OAO < CUO < TUO.

The band gaps increase in the sequence of CUO (1.43 eV) < CAO (1.58 eV) < TAO (1.61 eV) < OAO (1.63 eV) < TUO (1.74 eV). Meanwhile, the band gap values of CAO and TAO match the experimental values better than those of CUO and TUO, implying the random distribution of CH$_3$NH$_3$ molecule in cubic and tetragonal phases. In the case of optical properties, the tetragonal and orthorhombic phases possess similar peak energy levels of the dielectric function, absorption coefficients and reflectivity, while these levels are lower than those of cubic phases. Moreover, most optical absorption peaks of CUO and TUO move towards high energy levels compared to those of CAO and TAO. It is noteworthy that, among these studied structures, CUO has the lowest band gap of 1.43 eV and highest absorption coefficient. It is well acceptance that the ideal material for single-junction solar cells should have a band gap between 1.1 eV and 1.4 eV, and can absorb a wider range of visible light. Therefore, the CUO has a great potential as a photovoltaic application in the materials being studied. These results are expected to arouse the attentions on the effect of the CH$_3$NH$_3$ molecular orientations and promote the development of CH$_3$NH$_3$PbI$_3$ hybrid perovskites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mtcomm.2020.10.1816.

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[16] K.G. Stamplecoskie, J.S. Manser, P.V. Kamat, Dual nature of the excited state in inorganic–organic perovskite HC(NH$_3$)$_3$Pb$_x$Br$_{3-x}$ molecule may be determined combining near-edge X-ray absorption fine structures and grazing-incidence wide-angle X-ray scattering spectroscopy [55], and/or neutron scattering [56]. Therefore, the future studies should carefully consider the influence of not only the dopant but also the induced changes on the CH$_3$NH$_3$ molecular orientation, so as to effectively tailor the performance of the CH$_3$NH$_3$PbI$_3$ perovskite.

4. Conclusion

Electronic structures and optical properties as well. The orientation of the CH$_3$NH$_3$ molecule may be determined combining near-edge X-ray absorption fine structures and grazing-incidence wide-angle X-ray scattering spectroscopy [55], and/or neutron scattering [56]. Therefore, the future studies should carefully consider the influence of not only the dopant but also the induced changes on the CH$_3$NH$_3$ molecular orientation, so as to effectively tailor the performance of the CH$_3$NH$_3$PbI$_3$ perovskite. It is noteworthy that, among these studied structures, CUO has the lowest band gap of 1.43 eV and highest absorption coefficient. It is well acceptance that the ideal material for single-junction solar cells should have a band gap between 1.1 eV and 1.4 eV, and can absorb a wider range of visible light. Therefore, the CUO has a great potential as a photovoltaic application in the materials being studied. These results are expected to arouse the attentions on the effect of the CH$_3$NH$_3$ molecular orientations and promote the development of CH$_3$NH$_3$PbI$_3$ hybrid perovskites.


