Electronic and optical properties of orthorhombic (CH$_3$NH$_3$)BX$_3$ (B = Sn, Pb; X = F, Cl, Br, I) perovskites: a first-principles investigation†

Sean Nations,$^{a,b}$ Ting Jia,$^a$ Shengnian Wang$^{b,*}$ and Yuhua Duan$^{c,*a}$

Lead halide perovskites have generated considerable interest in solar cell, sensor, and electronics applications. While great focus has been placed on (CH$_3$NH$_3$)PbI$_3$, an organic–inorganic hybrid perovskite, comparatively little work has been done to understand some of its existing crystal phases and analogous materials after substituting with Sn and/or other halogens in the framework. Here, first-principles density functional theory calculations are performed to comprehensively evaluate the electronic and optical properties of (CH$_3$NH$_3$)BX$_3$ (B = Sn, Pb; X = F, Cl, Br, I) in a low-temperature orthorhombic phase. Bulk modulus, electronic structures, and several optical properties of these perovskite systems are further calculated. The obtained results are first confirmed by comparing with existing perovskite systems in literature. The shifting trends on those physical properties when extending to other barely studied systems of (CH$_3$NH$_3$)BX$_3$ is further revealed. The band gap of these perovskites is found to decrease when varying halogen anion in “X” sites from F to I, and/or substituting Pb cations with Sn in “B” sites. Notably, the less toxic Sn-containing perovskites, (CH$_3$NH$_3$)SnI$_3$ in particular, display higher absorption coefficients in the visible light range than their Pb-containing counterparts. An orthorhombic (CH$_3$NH$_3$)PbF$_3$ is predicted to exist at low temperature, and absorb strongly UV energy.

Our systematical examination efforts on the two groups of perovskites provide valuable physical insights in these materials, and the accompanied new findings warrant further investigation on such subjects.

1. Introduction

There is an ever-increasing environmental and social need to reduce carbon emissions which originate largely from fossil fuel burning. Utilizing clean and abundant solar energy by photovoltaic technologies is one major effort scientists are working on to accomplish these missions. Although silicon-based photovoltaic dominates current market share with an efficiency as high as ~21%, perovskites-based photovoltaics (PVs) demonstrates the fastest improvement on power conversion efficiency (PCE) in single-junction solar cells, reaching 25.2% in only ten years. Besides their promising PCE, perovskite thin films can be easily synthesized and integrated into devices and the prepared PVs also can tolerate much higher defect concentration than their Si-based counterparts. Besides their promising long-term solution to the climate crisis, perovskite materials can also play important roles in short-term solutions that make the current fossil fuel dominated energy supply greener.$^1$–$^3$ For example, the maintenance of appropriate fuel-to-air ratio can not only maximize combustion efficiency of fossil fuels, but also minimize the emission of toxic gases such as NO$_x$ to the environment. This requires gas sensors suitable for extreme environmental conditions (temperature, pressure, and potential exposure to free radicals).$^4$ The semiconductive and tunable optical properties of perovskite materials grant them interests as optical and photoelectrochemical sensors in combustion processes to detect ppm-range NO$_x$ signal in emission gas at high-temperature.$^5$–$^9$

In a common metal halide perovskite structure, ABX$_3$, A is an organic (e.g., methyl ammonium and formamidinium) or inorganic cation (e.g., cesium), B is a metal cation such as lead, and X is a halogen anion. One big drawback of such perovskite materials lies on the involvement of lead, which causes safety concerns during synthesis and applications. With similar valence electrons for bonding, tin is considered as a potential replacement for lead in the metal halide perovskite structure to mitigate toxicity.$^{10}$ Another challenge in perovskite applications comes from their short storage and operation lifetime. Perovskites face great stability and degradation issues when exposed to environmental (e.g., moisture, oxygen, and ultraviolet light), accompanied with consequent hygroscopicity, thermal instability, and ion migration issues.$^4$ Different degradation mechanisms are proposed, and great efforts have been made for their mitigations or solutions. One effective strategy is to replace elements in the ABX$_3$ structure of perovskite by partially

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$^*$(National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, Pennsylvania 15236, USA. E-mail: yuhua.duan@netl.doe.gov
$^a$Chemical Engineering Department, Louisiana Tech, University, Ruston, Louisiana 71272, USA. E-mail: swang@latech.edu
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substituting some majority halogen and/or metal ions or using their mixture, which could not only alleviate those stability issues, but also finely tune the electronic and optical properties of the perovskite crystals. For example, as the A site in perovskites is typically occupied by a larger cation than the B site, Pb and Sn containing perovskites normally have the A site occupied by these relatively large metal atoms. However, by selection of a comparatively large organic cation, the metal can be made to occupy the B position. An abnormally high absorption coefficient in the visible light range allows the material to function as a thin absorbing layer in photovoltaic cells to mitigate efficiency loss occurring mainly due to electron–hole recombination. These results have fueled hopes in perovskite applications and interests in new physical insights on the roles different metal and halide ions play in perovskite structure.

Another effective strategy comes from the retention of stable phases of perovskite crystals. Depending on the temperature, (MA)BX₃ (MA = CH₃NH₃; B = Sn, Pb; X = Cl, Br, I) perovskites exist in several different phases. At high temperatures, they are in the cubic phase (Pm3m). For example, the transition temperatures of (MA)PbX₃ (X = Cl, Br, I) are 177 K, 236 K, and 330 K respectively. Below these temperatures, (MA)PbX₃ perovskites stay in the tetragonal phase (I4/mcm). Under further low temperatures (i.e., below 172 K, 149–154 K, and 161 K for (MA)PbX₃ (X = Cl, Br, I respectively)), these perovskites are in the form of an orthorhombic phase (Pnma). In the literature, the electronic and optical properties of the high-temperature cubic phase (MA)BX₃ (B = Sn, Pb; X = Cl, Br, I) were widely studied both by computational calculations and experimental measurements. However, few studies look into these perovskites in their low-temperature phases, particularly the orthorhombic phase. One possible reason lies in the fact that many of these structures may only be stable at very low temperatures. Employing density functional theory (DFT), Ali et al. explored the structural, mechanical, electronic, and thermoelectric properties of the low-temperature orthorhombic perovskite phase of (MA)Pbl₃. They obtained a 1.57 eV band gap for (MA)Pbl₃ and found its lattice thermal conductivity is anisotropic, and the lattice thermal conductivity at 150 K was found to be 0.189, 0.138, and 0.530 W m⁻¹ K⁻¹ along the a, b, and c directions; however, there was no reporting on its optical properties. Using the non-local optB86b + vDW functional, Wang et al. predicted the crystal structure and band gap of (MA)PbI₃ in excellent agreement with experimental data. Using HSE06 hybrid functional approach, Feng and Xiao explored the effective masses and electronic and optical properties of orthorhombic (MA)SnX₃ (X = Cl, Br, and I) as solar energy absorbers. Their results indicated that both the effective masses and band gaps of (MA)SnX₃ perovskites decrease when the “X” sites change from chlorine to iodine, but their optical dielectric constants do not go down monotonically. No report was yet found in the literature on the structures and optical properties of (MA)BF₃ (B = Sn, Pb). Hence, a question arises if such structures could exist, even at low temperatures. Before we could evaluate the performance of perovskites (MA)BX₃ (MA = CH₃NH₃; B = Sn, Pb; X = F, Cl, Br, I) as either solar cell or sensor candidate materials, much work is still needed to be done to understand the electronic and optical properties of these perovskites in their stable phases at different temperatures. In this study, we performed extensive investigations on the electronic and optical properties of perovskite crystals of (MA)BX₃ in the low-temperature orthorhombic phase and make comparisons with the corresponding phases stable in high temperatures. This study serves as the first step to evaluate this organic–inorganic hybrid halide perovskite group in low-temperature phase to provide physical insights on their potentials.

2. Theoretical methods

Calculations here were performed via first-principles density functional theory (DFT), accomplished via the Vienna ab initio simulation package (VASP) using the plane-wave basis set and projector-augmented wave (PAW) method. Exchange and correlation effects were taken into account in a generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) functional. The cutoff energy for plan waves was 520 eV and the electronic energy convergence was set to 10⁻⁴ eV. As shown in Fig. 1, the unit cells of the orthorhombic phase (Z = 4) with space group Pnma (#62) were used to model all eight structures. K-point sampling grid of 9 × 6 × 9 was used to sample the (MA)PbX₃ and (MA)SnX₃ perovskites. The ionic positions were relaxed until the Hellmann–Feynman force on each atom was less than 0.01 eV Å⁻¹.

3. Results and discussion

3.1 Geometric and mechanical properties

The structures of (MA)BX₃ were first relaxed geometrically by minimizing their energies. We performed the optimizations for

![Image](https://via.placeholder.com/150)

**Fig. 1** The unit cell of (CH₃NH₃)BX₃ (B = Sn, Pb, X = F, Cl, Br, I) with Pnma (#62) nspace symmetry. Pink spheres are hydrogen atoms, brown ones are for carbon, light gray for nitrogen, purple for halides, and dark gray for metal Sn or Pb.
Table 1 The optimized crystal structures and volumes of orthorhombic (MA)BX₃ (B = Sn, Pb; X = F, Cl, Br, I) perovskites

| Perovskite | a (Å) | b (Å) | c (Å) | V (Å³) | E (eV per formula unit) |
|-----------|-------|-------|-------|--------|----------------------|
| (MA)SnF₃ | 6.3623 | 9.6369 | 11.3363 | 50.8212 | 456.67 | -59.13799 |
| (MA)SnCl₃ | 7.5518 [7.550] | 11.3363 [11.067] | 8.4178 [7.905] | 52.58994 | 989.10 [885.4] | -54.21088 |
| (MA)SnBr₃ | 7.9478 [7.813] | 11.8729 [11.546] | 8.7304 [8.144] | 54.41641 | 12.9027 [12.5804] | -52.58994 |
| (MA)SnI₃ | 8.5025 [8.326] | 12.6634 [12.428] | 9.1863 [8.556] | 59.39415 | (12.908) [12.964] | -50.82122 |
| (MA)PbF₃ | 6.3889 | 9.8163 | 7.4482 | 59.13799 | 50.94207 |
| (MA)PbCl₃ | 7.6084 | 11.5334 | 8.5135 | 472.72 | 747.23 | -52.75472 |
| (MA)PbBr₃ | 8.0029 | 12.0780 | 8.8423 | 854.70 | 1026.12 | -50.94207 |
| (MA)PbI₃ | 8.5353 [8.551] [8.555] | 12.9027 [12.5804] | (9.346) [9.250] | Overall, as one can see from Tables 1, 2 | | |

The optimized crystal structures and volumes of orthorhombic (MA)BX₃ (B = Sn, Pb; X = F, Cl, Br, I) perovskites.

Table 2 The calculated fractional coordinates of atoms in orthorhombic (MA)PbI₃. The corresponding data from Materials Project are given in brackets for comparison.

| Fractional coordinates | Element | x | y | z |
|------------------------|---------|---|---|---|
| H                      | 0.4977 [0.4943] | 0.3151 | 0.3146 | 0.858 [0.8570] |
| H                      | 0.4905 [0.4948] | 0.3197 [0.3192] | 0.119 [0.1201] |
| H                      | 0.3395 [0.3381] | 0.2500 | 0.2500 | 0.9198 [0.9214] |
| H                      | 0.6576 [0.6598] | 0.2500 | 0.2500 | 0.0526 [0.0503] |
| C                      | 0.5300 [0.5324] | 0.2500 | 0.2500 | 0.0624 [0.0622] |
| N                      | 0.4610 [0.4596] | 0.2500 | 0.2500 | 0.9149 [0.9151] |
| I                      | 0.8096 [0.8161] | 0.9735 [0.9779] | 0.3012 [0.3072] |
| I                      | 0.5404 [0.5377] | 0.2500 | 0.2500 | 0.4846 [0.4874] |
| Pb                     | 0.5000 [0.5000] | 0.0000 [0.0000] | 0.5000 [0.5000] | 0.0000 [0.0000] | 0.0000 [0.0000] |

Fig. 2 Energy versus volume for (MA)PbX₃ perovskites.
indicating a higher bulk modulus. This is confirmed by fitting the simulation data of the total energy (E) versus volume (V) in the form of Birch–Murnaghan equation of states (EOS) using eqn (1),

\[
E(V) = E_0 + \frac{9}{16} B_0 V_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right] \times B'_0 + \left[ \left( \frac{V_0}{V} \right)^{\frac{3}{2}} - 1 \right] \times \left[ 6 - 4 \times \left( \frac{V_0}{V} \right)^{\frac{3}{2}} \right] \]
\]

where a subscript of 0 indicates the equilibrium value of that parameter. \(B_0\) refers to the base-level bulk modulus, with \(B'_0\) referring to the first order variation of the bulk modulus, \(B\), with pressure, \(P\), all according to eqn (2).

\[
B = B_0 + B'_0 \times P
\]

The received parameters are listed in Table 3, together with the coefficients of determination of the regression fitting of the EOS models in those systems. Besides minimum fitting error, our bulk modulus result for (MA)PbI₃ (15 GPa) agrees well with the only available literature data (15.45 GPa in ref. 17). As halogen anion varies from F to Br in the X sites, the bulk modulus of perovskites decreases, which is consistent with observations from others. This can be attributed to the reduction of electronegativity when large halogen anions are present in the crystal. Smaller halogen anions in the X sites of perovskites provide larger resistance to the volume change, particularly to compression, as compared to larger halogens, due to the stronger interactions between protons and electrons. Such energy upshift from the equilibrium state is reflected in the fitting values of the bulk modulus change listed in Table 3. As for Sn and Pb in the B sites of the crystal structure, Sn-containing perovskites carry higher bulk moduli. The presence of Forbittals in Pb’s electronic configuration may enable more occupiable states for electrons. The changes of \(B\) values in our results reflect such lower energy deviations with an increase in pressure, while an outlier exists for I-containing perovskites, which have significantly different \(B'_0\) values than the other six perovskites examined.

### 3.2 Electronic structure properties

Due to the DFT approximations, which underestimate the excited state energies, the calculated band gap is usually smaller than the experimental measurement. The beyond-DFT methods are usually used to amend such band gap underestimations. As shown in Table 4, with the HSE06 functional approach, Feng and Xiao obtained larger band gaps of (MA)SnX₃ (X = Cl, Br, I). With inclusion of the GW many-body correction, Chiarella et al. calculated the band gaps of the cubic phase of two Sn-containing perovskites [(MA)SnCl₃: 3.44 eV; (MA)SnBr₃: 1.90 eV), which are relatively close to the experimental measured values of 3.69 eV and 2.15 eV respectively. Besides, Lang et al. reported that the spin-orbital

| Perovskite  | \(E_{\text{gap}}\) (eV) | SOC \(E_{\text{gap}}\) (eV) | \(E_{\text{form}}\) (eV per formula unit) |
|-------------|-----------------|-----------------|-----------------|
| (MA)SnF₃    | 2.325           | 2.122           | 0.11890         |
| (MA)SnCl₃   | 1.494 (1.94)    | 1.193           | −0.16782        |
| (MA)SnBr₃   | 1.186 (1.04)    | 0.804           | −0.18245        |
| (MA)SnI₃    | 0.969 (1.7)     | 0.520           | −0.12346        |
| (MA)PbF₃    | 3.466           | 2.651           | −0.17052        |
| (MA)PbCl₃   | 2.685           | 1.614           | −0.20019        |
| (MA)PbBr₃   | 2.265 (2.3)     | 1.171           | −0.18966        |
| (MA)PbI₃    | 2.030 (1.61)    | 0.808           | −0.14134        |

a From ref. 42. b From ref. 33. c From ref. 16. d From ref. 1. e From ref. 17. f From ref. 39.
coupling (SOC) could induce a band gap decrease of about 0.35 eV and 1.13 eV for B = Sn and Pb, respectively.

As SOC is known to be important for modeling electronic properties of heavier elements, the electronic structure properties of all orthorhombic (MA)BX₃ (B = Sn, Pb; X = F, Cl, Br, I) perovskites are further calculated by GGA + SOC. As an example, Fig. 3 shows the calculated band structure as well as the total and partial density of states (DOS) of (MA)PbCl₃, while that of the rest of the seven systems are provided in Fig. S2–S8 of the ESI.†

From Fig. 3(a) and S2(a)–S8(a),† the direct band gap nature of semiconductors is confirmed in these perovskites with their valence band maxima and conduction band minima located at the Γ point of the Brillouin zone. Table 4 summarizes our calculated band gaps of orthorhombic (MA)BX₃ (B = Sn, Pb; X = F, Cl, Br, I) perovskites, which are in good agreement with available theoretical results of (MA)PbI₃ and (MA)SnX₃ (X = Cl, Br, and I). Comparing with the GGA + PBE calculations without including SOC (2.685 eV for (MA)PbCl₃) shown in Fig. S9 of the ESI,† a much lower band gap (1.614 eV) was obtained (but still stay as direct band-gap semiconductors) which is consistent with the band-gap decrease predicted by Lang et al. In addition, the contribution of the p-orbitals is much lower when SOC is included. The calculated band gap values in Table 4 do show some deviations from the experimental data, with the results from the calculations including SOC being farther from experiment in most cases. Although the absolute values of the calculated band gaps vary with the adopted methods, their shifting trends when altering metal cations or halogen anions in these perovskites stays the same. The band gaps become smaller as large halogen and/or metal ions are included in the (MA)BX₃ structure as shown in Table 4, with the two most extreme cases of (MA)SnI₃ and (MA) PbF₃. When substituting Sn with Pb in B sites, larger band gaps are received for (MA)BX₃ with the same type of halogen.

From the total DOS (TDOS) and the partial DOS (PDOS) for each element in the (MA)BX₃ shown in Fig. 3(b) and S2(b)–S8(b),† it suggests that methyl ammonium ion contributes little
to the region around the Fermi level. Taking (MA)PbCl₃ as an example, the halogen Cl p-orbital contributes primarily to the valence band (VB) and the metal p-orbital to the conduction band (CB), as shown in the subpanels of Fig. 3(b). Cl has its p-orbital PDOS shifted to further above the Fermi energy, moving the relevant perovskites’ CBs in the same manner. Conversely, larger halogens appear to shift the CB closer to the Fermi energy (note: possibly by raising the Fermi energy). Drifting away from the Fermi energy enlarges the band gap, which explains why larger halogens appear to shift the CB closer to the Fermi energy, moving away from the Fermi energy, enlarging the band gap, which explains why larger halogens appear to shift the CB closer to the Fermi energy.

Based on the electronic structural properties, the formation energies ($E_{\text{form}}$) of orthorhombic (MA)BX₃ (B = Sn, Pb; X = F, Cl, Br, I) perovskites are evaluated by

$$E_{\text{form},\text{ABX}} = E_{0,\text{ABX}} - E_{0,\text{AX}} - E_{0,\text{BX}}$$  \hspace{1cm} (3)

where $E_{0,\text{ABX}}$ refers to the energy of a particular perovskite per formula unit as listed in Table 1, $E_{0,\text{AX}}$ refers to the energy per formulation of the (MA)X salt formed from the relevant halogen of the perovskite, and $E_{0,\text{BX}}$ refers to the energy per formulation of the BX₂ salt formed from the relevant halogen and metal of the perovskite. The calculated $E_{0,\text{AX}}$ and $E_{0,\text{BX}}$ are listed in Table S8 of the ESL† AX and BX₂ are important to reference against when quantifying thermodynamic stability as they are the phases typically in thermodynamic equilibrium with ABX₃ perovskites. The calculated $E_{\text{form}}$ of (MA)BX₃ perovskites are given in Table 4. The formation energy of all perovskites of (MA)BX₃ is negative in their orthorhombic phase, with an exception of (MA)SnF₃. This suggests that all seven perovskites could exist in $Pnma$ phase, including the least studied (MA)PbF₃. Unlike (MA)SnF₃, whose formation energy is positive, $Pnma$ phase (MA)PbF₃ perovskite could be favorable under low temperature conditions, although this has not yet been discovered experimentally to our best knowledge. To further verify the stability, additional computational work on the phonon properties of these fluorine-containing perovskites is needed to examine the stability and dynamics of their crystal structures.

### 3.3 Optical properties

To study the optical properties, the frequency-dependent dielectric matrix in the long wavelength limit ($q \rightarrow 0$) can be calculated using the sum over states approach. A brief description of our calculation methods is summarized here while detailed can be found in our previous publications. The formula for the imaginary part of the dielectric constant is a $3 \times 3$ Cartesian tensor:

$$
e_{2}^{\alpha\beta} = \frac{4\pi\varepsilon^{2}}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^{2}} \sum_{\gamma, k} \delta(E_{\gamma k} - E_{\alpha k} - \omega) \times \langle u_{\gamma k} + q \varepsilon \rangle u_{\gamma k} \langle u_{\gamma k} + q \varepsilon \rangle u_{\gamma k}^{*} \hspace{1cm} (4)$$

where the summation is over indices $\gamma$ (CB states), $\nu$ (VB states), and $k$ (k-points). $e$ is elementary charge, $\Omega$ is volume of the Brillouin zone, $\omega_k$ is weight of the $k$-point vector, $E_{\gamma k}$ and $E_{\alpha k}$ are energy levels, $u_{\gamma k}$ is the periodic portion of the orbital at $k$-point $k$. Vector $e_{\nu}$ is made of unit vectors for the Cartesian directions and $\alpha/\beta$ refer to axis $x, y,$ and $z$. From the imaginary part, the real part can be obtained by a Kramers–Kronig transformation.

$$
e_{1}^{\alpha\beta} = 1 + \frac{2}{\pi} P \int_{0}^{\infty} \frac{e_{2}^{\alpha\beta}(\omega)}{\omega^{2} - \omega_{0}^{2}} d\omega^{*} \hspace{1cm} (5)$$

By including SOC, Fig. 5 shows the calculated $e_{1}^{\alpha\beta}$ and $e_{2}^{\alpha\beta}$ versus wavelength for (MA)SnX₃ (X = F, Cl, Br, I). The results of (MA)PbX₃ (X = F, Cl, Br, I) are shown in Fig. S10 of the ESL† Due to the symmetrical and isotropic features of these crystals, the off-diagonal elements of dielectric tensor are zero and the diagonal elements ($\varepsilon_{xx}^{\alpha\beta}$, $\varepsilon_{yy}^{\alpha\beta}$, $\varepsilon_{zz}^{\alpha\beta}$) are close to each other, but not identical. As shown in Fig. 5, we take the average of these three diagonal elements as the overall dielectric constants in further
calculation of their optical properties. Comparing Fig. 5 with the results of the GGA + PBE calculations without including SOC shown in Fig. S11,† the main difference is seen in the imaginary dielectric constant, for which the heavier halogen perovskites do not fall off as quickly against wavelength.

As promising candidate materials in optical sensor applications, the most interesting wavelength range is from ultraviolet (UV) (10–400 nm) through the visible spectrum (400–800 nm) to near infrared and infrared (IR) (>800 nm), particularly, around the visible and near infrared range (~400 to 1000 nm).46 As shown in Fig. 5 and S9,† with halogen anions varying from F to I, both real and imaginary parts of the dielectric matrix in the frequency range of 400–1000 nm are increased. Other optical properties (e.g., the index of refraction, extinction coefficient, reflectivity, optical conductivity, absorption coefficient) derived from the dielectric matrix change correspondingly. According to eqn (4) and (5), the dielectric matrix depends on the differences of CB and VB states. When the halogen anion changes from F to I, the band gap of (MA)BX3 is decreased, as shown in Table 4. The small band gap slows down the decay of the imaginary portion of the dielectric constant. Therefore, (MA)SnI3 possesses higher \( \epsilon_{ad} \) over (MA)SnF3 with longer wavelength, as shown in Fig. 5. Similarly, when substituting Sn for Pb, the corresponding (MA)PbX3 possesses a higher band gap as shown in Table 4 and hence its dielectric matrix is smaller in comparison with that of (MA)SnX3. Comparing Fig. 5 with Fig. S10,† at visible light wavelength range (>400 nm), (MA)SnI3 has the highest \( \epsilon_{ad} \) and \( \epsilon_{ad} \) values while (MA)PbF3 possesses the lowest \( \epsilon_{ad} \) and \( \epsilon_{ad} \), which are consistent with trends of their electronic properties as described in Section 3.2.

Based on the calculated \( \epsilon_{ad} \) and \( \epsilon_{ad} \) values from eqn (4) and (5), the absorption coefficient, \( \alpha \), is further calculated at a particular wavelength, \( \lambda \), as shown in eqn (6).

\[
\alpha = \frac{2\sqrt{2\pi}}{\lambda} \left( (\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2)^{1/2}) \right)^{1/2} (6)
\]

where \( c \) refers to the speed of light. Other optical properties (e.g., index of refraction, extinction coefficient, reflectivity, optical conductivity, etc.) also can be derived from dielectric matrix and are provided in the ESL.† The calculated absorption coefficients of (MA)SnX3 and (MA)PbX3 are shown in Fig. 6(a) and S12 of the ESL,† respectively. Notably from these figures, perovskites containing heavier halogen anions exhibit higher absorption coefficients, particularly in the visible light range (400–800 nm) – a key parameter for both optical sensor and photovoltaic cell applications. Such shifts are a direct reflection of the change trends on their electronic structure properties. Despite Pb-containing perovskites’ prevalence over Sn counterparts, (MA)BCl3 (B = Sn, Pb) as an example, the Sn-containing perovskites display a higher absorption coefficient in the visible light range, as shown in Fig. 6(b). This suggests another important benefit the Sn-based perovskites could contribute to the performance improvement in the aforementioned applications besides their environmental benign advantages over the Pb-based counterparts.

Other optical properties such as extinction coefficient, index of refraction, and reflectivity are also calculated with detailed results placed in Fig. S13–S19 of the ESL.† From these results, similar change trends are also observed when varying the X site anions of perovskites from F to I and/or substituting Sn with Pb cations in the B sites. Hence, to achieve better optical performance (e.g., higher absorption coefficient) among orthorhombic perovskites (MA)BX3 (B = Sn, Pb; X = F, Cl, Br, I), our results suggest that (MA)SnX3 are better candidates than (MA)PbX3. Overall, with the same metal (Sn or Pb) cations, iodine anion contributes the strongest optical absorption among all halogen types while fluorine makes the least. As for high optical absorption performance in the visible light range, we predict that (MA)SnI3 is the best candidate while (MA)PbF3 is least favorable. However, (MA)PbF3, if stable, could serve in UV detection applications for its strong adsorption in the 10–400 nm range.

4. Conclusions

In this work, the electronic and optical properties of orthorhombic (MA)BX3 (B = Sn, Pb; X = F, Cl, Br, I) perovskites were calculated by first-principles density functional theory. The structures were relaxed to obtain the energy-minimized
geometry and formation energies. The bulk modulus was evaluated by fitting the Birch–Murnaghan equation-of-state and in good agreement with available data. Deviations from literature structure simulations exist, but a definite trend is still observed. Notably, the (MA)PbF₃ perovskite is found to have a negative formation energy, indicating its possible presence at low temperature conditions. The electronic structures of all eight perovskite systems were analyzed to evaluate the band gaps and contributors to the band gaps, with electronegativity suspected to be a major driving factor. Variations in the p-orbitals of the halogen anions is believed to decide the different levels in the valence band of these perovskite systems, and that of the metal cations contributing to the conduction band level. Hence, the band gaps of (MA)BX₃ are decreased with halogen element X varying from F to I, and larger band gaps are found in (MA)PbX₃ than corresponding (MA)SnX₃. Our calculations on the optical properties show the adsorption enhancement in the visible light range when the halogen anions vary from F to I, so does the substitution of Pb with Sn cation in the B sites, reflecting the similar trends as in the partial DOS shifting. Tin-based halide perovskites (particularly (MA)SnI₃) are shown to – among those examined – have comparably better absorbance of visible light energy, suggesting additional benefits in their replacement of the lead-based counterparts in broad perovskites applications.

Conflicts of interest

There are no conflicts to declare.

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