

# Structural and Electronic Properties of Inorganic Mixed Halide Perovskites

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In this work, we investigate the structural and electronic variations of all-inorganic mixed halide perovskites  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  upon their halide composition, by the first-principles calculation with the spin-orbit interaction. We find that these perovskites always keep their direct-bandgap nature, even though structurally their  $\text{PbX}_6$  octahedra are more or less distorted with different halide ratios (Cl/Br or Br/I). Their optical bowing parameters show no dependence on such composition ratios, which means their bandgaps can be linearly tuned. Moreover, these perovskites also exhibit rather good bipolar transport character, as both electrons and holes have the effective masses of less than  $0.2m_0$ . Therefore, we propose that by properly tuning the halide composition ratio, these mixed halide perovskites can be fabricated into light-emitting devices with selected frequency in a broad frequency range.

The organic–inorganic hybrid halide perovskites have attracted wide interests owing to their superior properties, such as high optical absorption coefficient, defect-tolerance, long diffusion length, and tunable bandgap by quantum-confined effect or chemical composition,<sup>[1–6]</sup> leading to the solar cell verified efficiency up to 22%.<sup>[7]</sup> Hybrid perovskites can also be applied to the optoelectronic devices including light-emitting diodes (LEDs), lasers, and photodetectors,<sup>[8–16]</sup> showing the excellent performance. Considering the similar structure, all-inorganic halide perovskites<sup>[17–25]</sup> have also been massively investigated to overcome the shortcomings of the hybrid halide perovskites.

The structure of organic–inorganic hybrid halide perovskites, with a chemical formula  $\text{ABX}_3$  (A for the organic cation; B for the inorganic cation;  $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ), can be represented as the spatial geometry, where B coordinated by X constructs the  $\text{BX}_6$  octahedron and A cation takes up the cavity between four adjacent core-sharing  $\text{BX}_6$  octahedron. By replacing the organic cation with Cs, Protesescu et al. have firstly synthesized colloidal

$\text{CsPbX}_3$  quantum dot with high quantum yield, stability, and narrow line-width.<sup>[19]</sup> At the same time, the halide anion-exchange process can be used to flexibly tune the electronic properties of  $\text{CsPbX}_3$ , realizing the entire visible spectral luminescence.<sup>[18,20]</sup> Through the anion-exchange process, the quantum dots<sup>[18–20]</sup> and nanoplatelets<sup>[22,25]</sup> are found to maintain the cubic phase. However, the radius difference of halide anions can make the local  $\text{PbX}_6$  octahedron distort gradually, resulting in the whole structural symmetry down.<sup>[26]</sup> And the broken symmetry can be reflected as the orthorhombic phase in the relatively low temperature.<sup>[27]</sup> Moreover, for the  $\text{CsPbX}_3$  nanowires, there may be either orthorhombic or cubic phase due to the similar diffraction patterns, which are also tuned by the halide ion exchange reaction.<sup>[28]</sup>

Therefore, the anion composition variation in the inorganic halide perovskites are proposed to inevitably change the electronic properties significantly. However, there are a few of theoretical understandings on the relationship between the electronic properties and the ratio of halide anions, which needs to be further expanded. For instance, the optical bowing parameter is used to describe the energy deviation between the experimental bandgap and the theoretical prediction from a linear fitting of the composition ratio. In the conventional semiconductor, such as  $\text{GaAs}_{1-x}\text{N}_x$ , the optical bowing parameter is giant and composition dependent.<sup>[29–32]</sup> However, the inorganic mixed halide perovskites<sup>[26,33]</sup> only show the small bowing parameter. But the detail information on that and the corresponding band structures versus the halide composition ratio is still lacking. Note that, theoretical studies on perovskites show that the DFT-GGA calculated bandgaps without spin–orbit interaction (SOI) are seemingly matched with the experimental values due to the error cancellation.<sup>[34,35]</sup> But, the band structures cannot be rightly described at the band edge without the SOI, especially for conduction band. The SOI will break the triply degenerate (CBM1-3) states into a double degenerate states and fourfold degenerate states.<sup>[36]</sup> Therefore, to understand the electronic properties of inorganic mixed halide perovskites properly, the SOI must be taken into account.

Herein we theoretically investigate the structural and electronic properties of both  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  perovskites including SOI. The formation energy of less than 20 meV per unit cell indicates the great possibility of synthesizing the inorganic perovskites with various ratio of halogens. The direct-bandgap nature can be preserved, even if

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the  $\text{PbX}_6$  octahedra have the different degree of distortion with varying the ratio of halogens. The calculated bandgap values of mixed halide perovskites are consistent well with the experimental observation, changing  $x$  from 0 to 1.<sup>[20]</sup> Furthermore, the quantitative optical bowing parameter is obtained in detail, which is a guide for precisely modulating the bandgap of inorganic mixed halide perovskites. The effective masses of both electrons and holes decrease from  $0.2m_0$  to  $0.08m_0$  along with increasing the ratio  $x$  in from  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  to  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$ . Our results show the great advantage of finely controlling the electronic properties of all-inorganic mixed halide perovskites, and assist in experimentally designing the high-performance optoelectronic devices, such as LEDs in a wide frequency range.

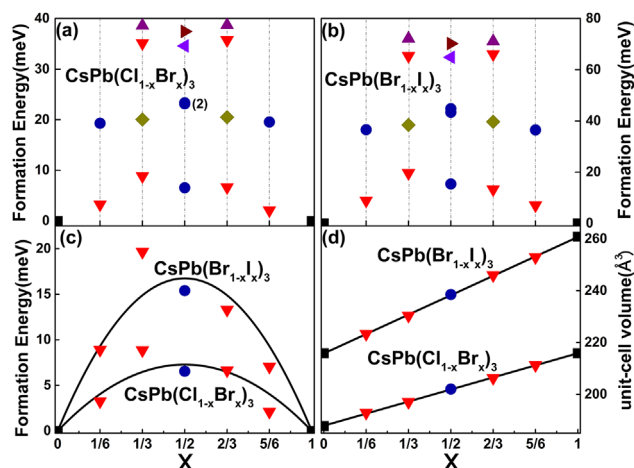
**Computational Method:** The calculations are performed based on density functional theory (DFT) with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)<sup>[37]</sup> as implemented in the Vienna Ab initio Simulation Package (VASP).<sup>[38,39]</sup> The ion cores are described by the projector augmented wave method<sup>[40,41]</sup> and the energy cutoff is set to 500 eV. The supercell approach with including  $1 \times 1 \times 2$  unit cell is used. The Brillouin zones are sampled with  $6 \times 6 \times 6$  k-point mesh for unit cell and  $6 \times 6 \times 3$  k-point mesh for supercell, respectively. The residual force on each atom is set to less than  $0.001 \text{ eV } \text{\AA}^{-1}$  in order to reach the optimized structures. The SOI is not included during the optimized process, since it can give the reasonable structures with remarkably reducing the computation cost. But for calculating the band structure, the SOI is taken into account.

Because the virtual-crystal approximation is not accurate to describe the properties of substitutional semiconductor alloys with strong SOI,<sup>[42]</sup> we choose the supercell method to investigate the mixed halide perovskites. The synthesized mixed halide perovskites by anion exchange reaction still keep the cubic crystallographic phase for nanocrystals and nanoplates at the room temperature.<sup>[18–20,22,25]</sup> The  $1 \times 1 \times 2$  cubic supercell of  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  are constructed to represent the possible structural models. After considering the symmetry condition, the number of the total structural configurations ( $2^6 = 64$ ) can be reduced to 19 with different mixed ratios for  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$ , respectively.

**Results and Discussion:** The formation energies of all configurations are calculated, according to the equation:

$$\Delta E(A_{1-x}B_x) = E(A_{1-x}B_x) - (1-x)E(A) - xE(B)$$

where  $A$ ,  $B$  represent  $\text{CsPbX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and  $A_{1-x}B_x$  stands for  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  or  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$ . **Figure 1a** and **b** demonstrate the formation energies of  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  under the different composition ratio  $x$ , respectively. It is found that the formation energies of the most stable  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  are less than 20 meV per unit cell for arbitrary composition ratio. Compared with the thermal energy at room temperature ( $k_B T = 26 \text{ meV}$ ), the inorganic mixed halide perovskites can be synthesized at room temperature or the relatively high temperature by anion-exchange experimental method.<sup>[18]</sup> Furthermore, **Figure 1c** shows the smallest formation energies are well fitting



**Figure 1.** The formation energies and space groups of (a)  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and (b)  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  with the different composition ratio  $x$  (square:  $\text{Pm}\bar{3}\text{m}$ ; up triangle:  $\text{P4}_2/\text{mmc}$ ; down triangle:  $\text{P4}/\text{mmm}$ ; left triangle:  $\text{P4mm}$ ; right triangle:  $\text{P}\bar{4}\text{m}2$ ; circle:  $\text{Pmmm}$ ; rhombus:  $\text{Pmm}2$ ). The formation energies and polynomial fit of (c) the most stable structures for  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$ . In (a), owing to the formation energies of two different  $\text{CsPb}(\text{Cl}_{0.5}\text{Br}_{0.5})_3$  structures being close to each other, we use the “(2)” to distinguish the cases. The unit-cell volumes (d) vary linearly as a function of the composition  $x$ .

with the second-order polynomials. The fitting curves follow the equation of  $\Delta E = \beta x(1-x)$  and the coefficients  $\beta$  (averaged per halogen atom) for  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  are about 0.029 and 0.067 eV, respectively.

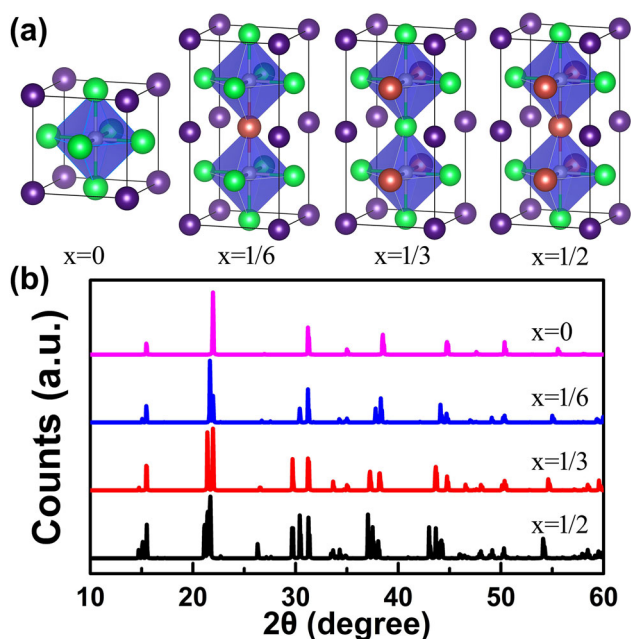
With variation of the ratio  $x$ , the symmetry of these mixed halide perovskites has gradually changed. The main factor, which causes the symmetry down and new space groups, might be the tilting of the strict  $\text{PbX}_6$  octahedron due to the nature ionic radius difference between halogens. **Figure 1d** shows that the unit-cell volume varies linearly as a function of the ratio  $x$ , which is in agreement with Vegard’s law. Finally, the most stable structures of different ratios are achieved according to the formation energies, which will be used below.

**Figure 2** presents the stable crystal structures and the simulated X-ray diffraction of  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  with  $x = 0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}$ . The rest of XRD spectrums (**Figure S1**, Supporting Information) are listed in the Supporting Information. The  $\text{CsPbCl}_3$  is cubic phase ( $\text{Pm}\bar{3}\text{m}$ ), while  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  with  $x = \frac{1}{6}, \frac{1}{3}$  and  $x = \frac{1}{2}$  are tetragonal phase ( $\text{P4}/\text{mmm}$ ) and orthorhombic phase ( $\text{Pmmm}$ ), respectively.

It is observed that the  $\text{PbX}_6$  octahedral distortion plays a key role in phase transition. Therefore, we quantitatively calculate the degree of the  $\text{PbX}_6$  octahedral distortion ( $\Delta d$ ) according to the equation<sup>[43]</sup>:

$$\Delta d = \frac{1}{6} \sum_{n=1}^6 \left[ \frac{d_n - d}{d} \right]^2$$

where we set  $d$  as the average  $\text{Pb-X}$  bond length and  $d_n$  is the bond length of the  $\text{Pb-X}_n$ . Table S1, Supporting Information shows the detail average bond length and octahedral distortion ( $\Delta d$ ), where the bond length gradually increases



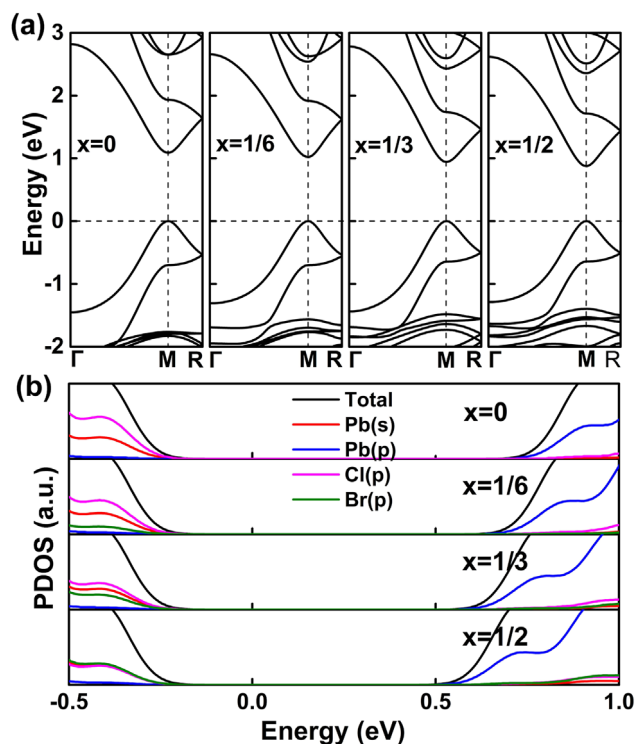
**Figure 2.** The (a) atomic structures and (b) XRD patterns of CsPb-(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, with  $x = 0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}$ , corresponding to the lowest formation energy for different mixed ratios (violet: Cs; gray: Pb; green: Cl; brown: Br).

from Cl to I and the  $\Delta d$  gets the maximum with Cl:Br or Br:I equal to 1:1. Compared with two dimensional corrugated  $\alpha$ -(DMEN)PbBr<sub>4</sub> octahedral transformation,<sup>[43]</sup> the structural distortion's degree in the inorganic mixed halide perovskites is relatively less. The structural distortion stems from the nature of chemical composition, e.g., the ionic radius of Cl<sup>-</sup> is smaller than that of Br<sup>-</sup> (Cl<sup>-</sup>, 1.81 Å; Br<sup>-</sup>, 1.96 Å).<sup>[18]</sup> When we insert Br<sup>-</sup> into the Cl<sup>-</sup>-based pure phase, the different bond length between Pb-Cl and Pb-Br causes the structural distortion, following with the lattice constant (LC) of CsPb-(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> gradually expanded, as presented in Table S1, Supporting Information. With the lattice stretching, the internal strain of structure have relaxed, leading to the less energy for synthesizing the mixed phase.

The structural variation of the inorganic mixed halide perovskites is the evidence of reflecting the halide composition ratio  $x$ , which can be observed from the XRD pattern. Figure 2b shows the simulated XRD pattern of CsPb(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>. The single peak close to 20 or 30° splits into the new peaks because of the symmetry broken as the concentration of Br increasing. Overall, during halide anion exchange, all peaks (Figure S1, Supporting Information) have the obvious tendency to move to the low angle. For example, when Br replaces the center Cl in the CsPbCl<sub>3</sub> supercell as shown in Figure 2a, the  $z$ -orientated Pb-Cl bonds become the longer Pb-Br bonds, making the LC in  $z$  direction elongate. For the  $x$  or  $y$  direction, the LC has little change. As a result, the single peak splits into multiple peaks. Obviously, the LC of CsPb(Cl<sub>0.5</sub>Br<sub>0.5</sub>)<sub>3</sub> is totally anisotropic with the largest number of splitting peaks. Further, these whole varied trend of simulated XRD results is closed to the experimental results,<sup>[18–20]</sup> where all peaks are also shifted to the low angle.

In order to find the influence of octahedral distortion  $\Delta d$ , we further calculate band structures and projected density of states (PDOS) of the inorganic mixed halide perovskites with SOI. In the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, it is found that the PbI<sub>6</sub> octahedral distortion because of the molecular cation vibration or rotations, can make the transition from direct to indirect bandgap.<sup>[35]</sup> But, as described in Figure 3 and Figure S5, Supporting Information the direct transition character is still preserved even if the octahedral distortion is induced by mixing the halide anions. Therefore, it may realize the high radiative recombination rate for fabricating LEDs with the high quantum yield (QY). Moreover, the Rashba effect, namely, the spin splitting due to the structural inversion asymmetry, is not observed in the inorganic perovskites. Though the calculated bandgaps are underestimated, the bandgaps gradually decrease along with increasing the bromine's incorporation, which is in good agreement with experimental and theoretical results.<sup>[20,26]</sup> The PDOS can be used to understand the origin behind the tendency of bandgap variation. Figure 3b shows that the valence band maximum (VBM) consists of  $p$  orbital of halogens and  $s$  orbital of Pb, while the conduction band minimum (CBM) is mainly derived from the  $p$  orbital of Pb. Therefore, the decrease of the bandgap mainly originates from uplifting the VBM, in which the  $p$  orbital of halogens raises in energy from Cl, Br to I.

The effective masses of both electrons and holes are calculated along R-M (001), R- $\Gamma$  (111), and M- $\Gamma$  (110), as shown in Table 1. It is observed that the composition  $x$  has a strong influence on the effective mass. Compared with the results without SOI, most of



**Figure 3.** The (a) band structures and (b) projected density of state (PDOS) of CsPb(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, with  $x = 0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}$ . The high symmetry k-points are  $\Gamma$  (0.0, 0.0, 0.0), M (0.5, 0.5, 0.0), and R (0.5, 0.5, 0.5).

**Table 1.** The calculated bandgaps (BG) (unit: eV) and effective masses (unit:  $m_0$ ) of all-inorganic mixed halide perovskites along R- $\Gamma$  (111), M- $\Gamma$  (110), and R-M (001) with/without SOC.

|                                         | GGA   |             |       |             |       |       | GGA + SOC |       |             |       |             |       |       |       |
|-----------------------------------------|-------|-------------|-------|-------------|-------|-------|-----------|-------|-------------|-------|-------------|-------|-------|-------|
|                                         | BG    | R- $\Gamma$ |       | M- $\Gamma$ |       | R-M   |           | BG    | R- $\Gamma$ |       | M- $\Gamma$ |       | R-M   |       |
|                                         |       | $m_h$       | $m_e$ | $m_h$       | $m_e$ | $m_h$ | $m_e$     |       | $m_h$       | $m_e$ | $m_h$       | $m_e$ | $m_h$ | $m_e$ |
| CsPbCl <sub>3</sub>                     | 2.200 | 0.222       | 0.336 |             |       | 0.224 | 0.978     | 1.081 | 0.192       | 0.203 |             |       | 0.191 | 0.198 |
| CsPbCl <sub>2.5</sub> Br <sub>0.5</sub> | 2.050 |             |       | 0.227       | 1.017 | 0.193 | 0.113     | 1.021 |             |       | 0.194       | 0.209 | 0.165 | 0.162 |
| CsPbCl <sub>2</sub> Br <sub>1</sub>     | 1.881 | 0.160       | 0.194 |             |       | 0.181 | 0.98      | 0.936 | 0.172       | 0.179 |             |       | 0.192 | 0.209 |
| CsPbCl <sub>1.5</sub> Br <sub>1.5</sub> | 1.859 |             |       | 0.202       | 0.178 | 0.200 | 0.928     | 0.876 |             |       | 0.163       | 0.166 | 0.163 | 0.169 |
| CsPbCl <sub>1</sub> Br <sub>2</sub>     | 1.827 | 0.193       | 0.284 |             |       | 0.237 | 1.015     | 0.798 | 0.156       | 0.156 |             |       | 0.194 | 0.212 |
| CsPbCl <sub>0.5</sub> Br <sub>2.5</sub> | 1.809 |             |       | 0.178       | 0.197 | 0.208 | 0.904     | 0.739 |             |       | 0.137       | 0.133 | 0.162 | 0.166 |
| CsPbBr <sub>3</sub>                     | 1.785 | 0.182       | 0.268 |             |       | 0.181 | 0.894     | 0.670 | 0.139       | 0.134 |             |       | 0.134 | 0.129 |
| CsPbBr <sub>2.5</sub> I <sub>0.5</sub>  | 1.667 |             |       | 0.187       | 0.928 | 0.159 | 0.086     | 0.611 |             |       | 0.139       | 0.132 | 0.110 | 0.103 |
| CsPbBr <sub>2</sub> I <sub>1</sub>      | 1.547 | 0.173       | 0.205 |             |       | 0.191 | 0.985     | 0.543 | 0.124       | 0.116 |             |       | 0.136 | 0.129 |
| CsPbBr <sub>1.5</sub> I <sub>1.5</sub>  | 1.540 |             |       | 0.170       | 0.144 | 0.173 | 0.881     | 0.494 |             |       | 0.114       | 0.104 | 0.112 | 0.101 |
| CsPbBr <sub>1</sub> I <sub>2</sub>      | 1.518 | 0.167       | 0.222 |             |       | 0.206 | 0.950     | 0.432 | 0.101       | 0.098 |             |       | 0.138 | 0.124 |
| CsPbBr <sub>0.5</sub> I <sub>2.5</sub>  | 1.501 |             |       | 0.153       | 0.151 | 0.182 | 0.850     | 0.376 |             |       | 0.092       | 0.080 | 0.110 | 0.095 |
| CsPbI <sub>3</sub>                      | 1.482 | 0.156       | 0.206 |             |       | 0.155 | 0.837     | 0.312 | 0.096       | 0.081 |             |       | 0.083 | 0.071 |

the effective masses including SOI are slightly reduced and the  $m_e$  along R-M reduces remarkably. We find that the effective mass  $m_e$  and  $m_h$  with SOI ranges from 0.21 to 0.07 $m_0$  and from 0.19 to 0.08 $m_0$ , respectively. Our calculated effective masses in CsPbX<sub>3</sub> (X = Cl, Br, I) are in agreement with the previous work.<sup>[19]</sup> The effective masses in the mixed halide perovskites are comparable to or significantly smaller than the effect mass  $m_t(e) = 0.19m_3^{[44]}$  or  $m_l(h) = 0.16m_0^{[45]}$  of silicon. Moreover, the effective masses in CsPbI<sub>3</sub> is also smaller than that in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The effective mass along R- $\Gamma$  in CsPbI<sub>3</sub> is  $m_h = 0.096m_0$  and  $m_e = 0.081m_0$ , while in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, it is  $m_h = 0.29m_0$  and  $m_e = 0.23m_0$  with SOI<sup>[46]</sup> and  $m_h = 0.18m_0$  and  $m_e = 0.15m_0$  with GW + SOI.<sup>[47]</sup> The experimental reduced effective mass in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is 0.104 $m_0$ ,<sup>[48]</sup> which is also larger than our prediction in CsPbI<sub>3</sub>. The small effective masses of the inorganic mixed halide perovskites are of great benefit to the devices with high-performance carrier transport, especially bipolar transport.

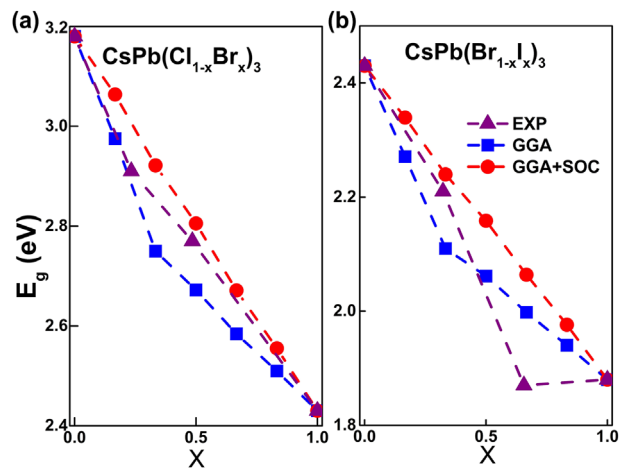
Since the bandgaps are underestimated due to the nature of the DFT-GGA, a correction is applied to the bandgaps of the mixed halide perovskites with the equation of

$$\Delta E_g(A_{1-x}B_x) = (1-x)\Delta E_g(A) + x\Delta E_g(B)$$

where  $\Delta E_g(A_{1-x}B_x)$  is the bandgap correction of CsPb(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> or CsPb(Br<sub>1-x</sub>I<sub>x</sub>)<sub>3</sub>,  $\Delta E_g(A)$  and  $\Delta E_g(B)$  is the energy shift for matching the experimental values of CsPbX<sub>3</sub> for Cl and Br or Br and I, respectively. **Figure 4** shows the bandgaps of the inorganic mixed halide perovskites with/without SOI and the corresponding experimental measurements.<sup>[20]</sup> It is found that the values with SOI are better matched with the experimental measurement but the values without SOI is not. Therefore, the SOI is non-ignorable and important to accurately describe the tendency of bandgaps of inorganic mixed halide perovskites.

In general, the bandgaps in these material show an obvious linear relationship with the concentration  $x$ . However, the

experimental bandgap of Cs<sub>0.9</sub>PbBr<sub>1.1</sub>I<sub>2.1</sub><sup>[20]</sup> is remarkably smaller than the prediction. This result is possibly attributed to the phase separation. Experimentally, the sizes of the synthesized CsPbBr<sub>x</sub>I<sub>3-x</sub> nanoparticles are about 9 nm,<sup>[20]</sup> where the quantum confinement effect of them larger than 7 nm can be neglected.<sup>[49]</sup> Recently, in mixed halide perovskite CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3-x</sub>I<sub>x</sub> the phase separation can be measured at the grain boundary under the light illumination, which makes the photoluminescence peak red shift.<sup>[50]</sup> In this case, the Cs<sub>0.9</sub>PbBr<sub>1.1</sub>I<sub>2.1</sub> may be similarly transferred to the physical mixer of CsPbBr<sub>3</sub> and CsPbI<sub>3</sub>, where the peak is from the CsPbI<sub>3</sub>. Therefore, the bandgap of Cs<sub>0.9</sub>PbBr<sub>1.1</sub>I<sub>2.1</sub> is close to the bandgap of CsPbI<sub>3</sub>.



**Figure 4.** Bandgaps of (a) CsPb(Cl<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> and (b) CsPb(Br<sub>1-x</sub>I<sub>x</sub>)<sub>3</sub> based on the GGA with/without spin-orbit coupling. Applying the bandgap correction, we get the mixed ratio bandgaps of inorganic mixed halide perovskites compared to the experimental results.<sup>[20]</sup>

To further find the relationship between the bandgaps and the halide composition  $x$ , we have calculated the optical bowing parameter. The optical bowing parameter is to evaluate the deviation between the bandgaps of inorganic mixed halide perovskites and the composition-linearly-fitting bandgaps, which is expressed as<sup>[29–31]</sup>

$$\Delta E_g(x) = bx(x-1) = E_g(x) - [(1-x)E_g(A) + xE_g(B)]$$

where  $b$  is the bowing parameter,  $E_g(A)$  and  $E_g(B)$  are the bandgaps of the pure A and B, respectively, and the  $E_g(x)$  is the bandgap of A, B mixed halide perovskites with the composition  $x$ . Table S2, Supporting Information shows their optical bowing parameters under the different composition ratios without/with SOI. The optical bowing parameter is about hundreds of meV without SOI, while it is one order of magnitude smaller, about tens of meV with SOI. Considering the excellent prediction on the experimental bandgaps with SOI, the small optical bowing parameter indicates that the bandgaps of inorganic mixed halide perovskites can be accurately and linearly tuned by changing the composition ratio of halogens. Unlike the conventional  $\text{GaAs}_{1-x}\text{N}_x$  alloys owing giant bowing coefficient,<sup>[31,32]</sup> the optical bowing parameter in the inorganic mixed halide perovskites is small. Because of the band characters of  $\text{CsPbX}_3$ , the reduced symmetry can decrease the intraband interaction in the VB and increase the interband interaction in both VB and CB.<sup>[26]</sup> Both of the interactions lead to the small optical bowing parameter in these mixed halide cases. From the band structures of these perovskites as shown in Supporting Information, the CBM of pure perovskites is three degeneracy without SOI. This degeneracy will be lifted when the symmetry is reduced by incorporating new halogens. Therefore, without SOI, the bandgap will vary along with not only the halide composition, but also structural symmetry reduction, resulting in the off-linear variation of bandgaps. However, including SOI, the CBM degeneracy of pure perovskites is lifted initially. The bandgap varies only along with the halide composition, showing a good linear fitting with the halide composition.

In summary, we have theoretically investigated the structural and electronic properties of the inorganic mixed halide perovskites of  $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$  and  $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$  based on the first-principles DFT calculation. We find that only with the SOI the DFT results can present reliably the electronic properties of these halide perovskites, in predicting correctly their experimental bandgap values of diverse composition values. With such reliable DFT results, we reveal a few fundamental electronic characters of these inorganic perovskites in optoelectronic applications. Firstly, these inorganic perovskites always keep their direct-bandgap nature, despite the introduced structural distortion of the  $\text{PbX}_6$  octahedra, that means these mixed halide perovskites can be made into good light-emitter with high QY. Moreover, their optical bowing parameter is composition independent, which shows such perovskites can be flexibly realized into the LEDs with the desired working wavelength in a wide frequency range ( $>1\text{ eV}$ ). Furthermore, these perovskites also exhibit the bipolar transport character, whose effective mass for both electrons and holes is no more than  $0.2m_0$ . Therefore, by properly tuning their halide composition ratio, these inorganic mixed halide perovskites

can be fabricated into desired light-emitting devices with selected frequency in a broad frequency range.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

band structure, density functional theory, inorganic mixed halide perovskites, optical bowing parameter

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