Supplementary Materials

Computational Investigation of the Folded and Unfolded Band Structure and Structural and Optical Properties of Inorganic Perovskite

Hamid M. Ghaithan [1,2,*], Zeyad. A. Alahmed [1,*], Andreas Lyras [1], Saif M. H. Qaid [1] and Abdullah S. Aldwayyan [1,3,4,*]

[1]Physics and Astronomy Department, College of Science, King Saud University, P.O. Box 2455, Riyadh, 11451, Saudi Arabia.

[2]Physics Department, College of Education and linguistic, Amran University, Amran 2915, Yemen.

[3]King Abdullah Institute for Nanotechnology, King Saud University, P.O. Box 2454, Riyadh 11451, Saudi Arabia.

[4]K.A.CARE Energy Research and Innovation Center at Riyadh, P.O. Box 2022, Riyadh 11454, Saudi Arabia.

* Correspondence: hghaithan@ksu.edu.sa, zalahmed@ksu.edu.sa and dwayyan@ksu.edu.sa

Structural properties of $CsPb(I_{1-x}Br_x)_3$ Perovskite

Table S1

$CsPbI_3$

Lattice type P
Space group name P 1
Space group number 1
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
6.28000	6.28000	25.12000	90.0000	90.0000	90.0000

Unit-cell volume = 990.692707 Å^3

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Cs	Cs1	0.00000	0.00000	0.00000	1.000	1.000	1a	1
2	Cs	Cs2	0.00000	0.00000	0.25000	1.000	1.000	1a	1
3	Cs	Cs3	0.00000	0.00000	0.50000	1.000	1.000	1a	1
4	Cs	Cs4	0.00000	0.00000	0.75000	1.000	1.000	1a	1
5	Pb	Pb1	0.50000	0.50000	0.12500	1.000	1.000	1a	1
6	Pb	Pb2	0.50000	0.50000	0.37500	1.000	1.000	1a	1
7	Pb	Pb3	0.50000	0.50000	0.62500	1.000	1.000	1a	1
8	Pb	Pb4	0.50000	0.50000	0.87500	1.000	1.000	1a	1
9	I	I1	0.50000	0.50000	0.00000	1.000	1.000	1a	1
10	I	I2	0.00000	0.50000	0.12500	1.000	1.000	1a	1
11	I	I3	0.50000	0.00000	0.12500	1.000	1.000	1a	1
12	I	I4	0.50000	0.50000	0.25000	1.000	1.000	1a	1
13	I	I5	0.00000	0.50000	0.37500	1.000	1.000	1a	1
14	I	I6	0.50000	0.00000	0.37500	1.000	1.000	1a	1
15	I	I7	0.50000	0.50000	0.50000	1.000	1.000	1a	1
16	I	I8	0.00000	0.50000	0.62500	1.000	1.000	1a	1
17	I	I9	0.50000	0.00000	0.62500	1.000	1.000	1a	1
18	I	I10	0.50000	0.50000	0.75000	1.000	1.000	1a	1
19	I	I11	0.00000	0.50000	0.87500	1.000	1.000	1a	1
20	I	I12	0.50000	0.00000	0.87500	1.000	1.000	1a	1

Table S2

$CsPb(I_{0.75}Br_{0.25})_3$

Lattice type P
Space group name P 1
Space group number 1
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
6.17750	6.17750	24.71000	90.0000	90.0000	90.0000

Unit-cell volume = 942.970715 Å^3

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Cs	Cs1	0.00000	0.00000	0.00000	1.000	1.000	1a	1
2	Cs	Cs2	0.00000	0.00000	0.25000	1.000	1.000	1a	1
3	Cs	Cs3	0.00000	0.00000	0.50000	1.000	1.000	1a	1
4	Cs	Cs4	0.00000	0.00000	0.75000	1.000	1.000	1a	1
5	Pb	Pb1	0.50000	0.50000	0.12500	1.000	1.000	1a	1
6	Pb	Pb2	0.50000	0.50000	0.37500	1.000	1.000	1a	1
7	Pb	Pb3	0.50000	0.50000	0.62500	1.000	1.000	1a	1
8	Pb	Pb4	0.50000	0.50000	0.87500	1.000	1.000	1a	1
9	Br	Br1	0.50000	0.50000	0.00000	1.000	1.000	1a	1
10	I	I1	0.00000	0.50000	0.12500	1.000	1.000	1a	1
11	I	I2	0.50000	0.00000	0.12500	1.000	1.000	1a	1
12	I	I3	0.50000	0.50000	0.25000	1.000	1.000	1a	1
13	Br	Br2	0.00000	0.50000	0.37500	1.000	1.000	1a	1
14	I	I4	0.50000	0.00000	0.37500	1.000	1.000	1a	1
15	I	I5	0.50000	0.50000	0.50000	1.000	1.000	1a	1
16	I	I6	0.00000	0.50000	0.62500	1.000	1.000	1a	1
17	Br	Br3	0.50000	0.00000	0.62500	1.000	1.000	1a	1
18	I	I7	0.50000	0.50000	0.75000	1.000	1.000	1a	1
19	I	I8	0.00000	0.50000	0.87500	1.000	1.000	1a	1
20	I	I9	0.50000	0.00000	0.87500	1.000	1.000	1a	1

Table S3

$CsPb(I_{0.5}Br_{0.5})_3$

Lattice type P
Space group name P 1
Space group number 1
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
6.07500	6.07500	24.30000	90.0000	90.0000	90.0000

Unit-cell volume = 896.806603 Å^3

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Cs	Cs1	0.00000	0.00000	0.00000	1.000	1.000	1a	1
2	Cs	Cs2	0.00000	0.00000	0.25000	1.000	1.000	1a	1
3	Cs	Cs3	0.00000	0.00000	0.50000	1.000	1.000	1a	1
4	Cs	Cs4	0.00000	0.00000	0.75000	1.000	1.000	1a	1
5	Pb	Pb1	0.50000	0.50000	0.12500	1.000	1.000	1a	1
6	Pb	Pb2	0.50000	0.50000	0.37500	1.000	1.000	1a	1
7	Pb	Pb3	0.50000	0.50000	0.62500	1.000	1.000	1a	1
8	Pb	Pb4	0.50000	0.50000	0.87500	1.000	1.000	1a	1
9	Br	Br1	0.50000	0.50000	0.00000	1.000	1.000	1a	1
10	I	I1	0.00000	0.50000	0.12500	1.000	1.000	1a	1
11	Br	Br2	0.50000	0.00000	0.12500	1.000	1.000	1a	1
12	I	I2	0.50000	0.50000	0.25000	1.000	1.000	1a	1
13	Br	Br3	0.00000	0.50000	0.37500	1.000	1.000	1a	1
14	I	I3	0.50000	0.00000	0.37500	1.000	1.000	1a	1
15	Br	Br4	0.50000	0.50000	0.50000	1.000	1.000	1a	1
16	I	I4	0.00000	0.50000	0.62500	1.000	1.000	1a	1
17	Br	Br5	0.50000	0.00000	0.62500	1.000	1.000	1a	1
18	I	I5	0.50000	0.50000	0.75000	1.000	1.000	1a	1
19	Br	Br6	0.00000	0.50000	0.87500	1.000	1.000	1a	1
20	I	I6	0.50000	0.00000	0.87500	1.000	1.000	1a	1

Table S4

$CsPb(I_{0.25}Br_{0.75})_3$

Lattice type P
Space group name P 1
Space group number 1
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
5.97250	5.97250	23.89000	90.0000	90.0000	90.0000

Unit-cell volume = 852.174301 Å^3

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Cs	Cs1	0.00000	0.00000	0.00000	1.000	1.000	1a	1
2	Cs	Cs2	0.00000	0.00000	0.25000	1.000	1.000	1a	1
3	Cs	Cs3	0.00000	0.00000	0.50000	1.000	1.000	1a	1
4	Cs	Cs4	0.00000	0.00000	0.75000	1.000	1.000	1a	1
5	Pb	Pb1	0.50000	0.50000	0.12500	1.000	1.000	1a	1
6	Pb	Pb2	0.50000	0.50000	0.37500	1.000	1.000	1a	1
7	Pb	Pb3	0.50000	0.50000	0.62500	1.000	1.000	1a	1
8	Pb	Pb4	0.50000	0.50000	0.87500	1.000	1.000	1a	1
9	I	I1	0.50000	0.50000	0.00000	1.000	1.000	1a	1
10	Br	Br1	0.00000	0.50000	0.12500	1.000	1.000	1a	1
11	Br	Br2	0.50000	0.00000	0.12500	1.000	1.000	1a	1
12	Br	Br3	0.50000	0.50000	0.25000	1.000	1.000	1a	1
13	I	I2	0.00000	0.50000	0.37500	1.000	1.000	1a	1
14	Br	Br4	0.50000	0.00000	0.37500	1.000	1.000	1a	1
15	Br	Br5	0.50000	0.50000	0.50000	1.000	1.000	1a	1
16	Br	Br6	0.00000	0.50000	0.62500	1.000	1.000	1a	1
17	I	I3	0.50000	0.00000	0.62500	1.000	1.000	1a	1
18	Br	Br7	0.50000	0.50000	0.75000	1.000	1.000	1a	1
19	Br	Br8	0.00000	0.50000	0.87500	1.000	1.000	1a	1
20	Br	Br9	0.50000	0.00000	0.87500	1.000	1.000	1a	1

Table S5

$CsPbBr_3$

Lattice type P
Space group name P 1
Space group number 1
Setting number 1

Lattice parameters

a	b	c	alpha	beta	gamma
5.87000	5.87000	23.48000	90.0000	90.0000	90.0000

Unit-cell volume = 809.047965 Å^3

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Cs	Cs1	0.00000	0.00000	0.00000	1.000	1.000	1a	1
2	Cs	Cs2	0.00000	0.00000	0.25000	1.000	1.000	1a	1
3	Cs	Cs3	0.00000	0.00000	0.50000	1.000	1.000	1a	1
4	Cs	Cs4	0.00000	0.00000	0.75000	1.000	1.000	1a	1
5	Pb	Pb1	0.50000	0.50000	0.12500	1.000	1.000	1a	1
6	Pb	Pb2	0.50000	0.50000	0.37500	1.000	1.000	1a	1
7	Pb	Pb3	0.50000	0.50000	0.62500	1.000	1.000	1a	1
8	Pb	Pb4	0.50000	0.50000	0.87500	1.000	1.000	1a	1
9	Br	Br1	0.50000	0.50000	0.00000	1.000	1.000	1a	1
10	Br	Br2	0.00000	0.50000	0.12500	1.000	1.000	1a	1
11	Br	Br3	0.50000	0.00000	0.12500	1.000	1.000	1a	1
12	Br	Br4	0.50000	0.50000	0.25000	1.000	1.000	1a	1
13	Br	Br5	0.00000	0.50000	0.37500	1.000	1.000	1a	1
14	Br	Br6	0.50000	0.00000	0.37500	1.000	1.000	1a	1
15	Br	Br7	0.50000	0.50000	0.50000	1.000	1.000	1a	1
16	Br	Br8	0.00000	0.50000	0.62500	1.000	1.000	1a	1
17	Br	Br9	0.50000	0.00000	0.62500	1.000	1.000	1a	1
18	Br	Br10	0.50000	0.50000	0.75000	1.000	1.000	1a	1
19	Br	Br11	0.00000	0.50000	0.87500	1.000	1.000	1a	1
20	Br	Br12	0.50000	0.00000	0.87500	1.000	1.000	1a	1

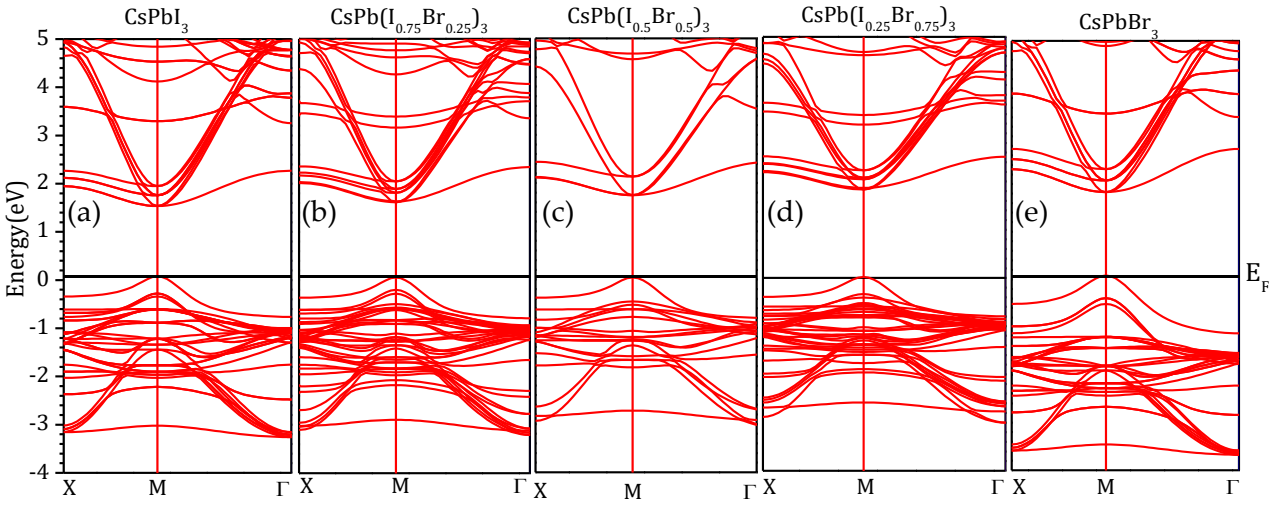

Figure S1. (a-e) Calculated the band structures of $CsPbI_3$, $CsPb(I_{0.75}Br_{0.25})_3$, $CsPb(I_{0.5}Br_{0.5})_3$, $CsPb(I_{0.25}Br_{0.75})_3$, and $CsPbBr_3$ using the PBE-GGA method.

Fold2Bloch package

This program is intended to unfold the first-principle band structure of supercells obtained with WIEN2k. It computed the Bloch spectral weight, which amounts to a Bloch k-character of the particular energy eigenstates. It is implied that the supercell is constructed from the primitive unit cell by repeating it NX, NY, NZ times along the corresponding axes. This information is also used for unfolding. The spectral weight is computed based on the plane wave coefficients read from a vector-file. Results of the calculations a stored in the file **case.f2b**, which contains the unfolded k-points, eigenvalues and the Bloch weights. Since the obtained band structure is somewhat different from the regular one, a set of utilities is provided in order to assist with visualization [1].

The spectral weight (SW) $\omega_n(k)$ amounts to a Bloch k-character of the n'th energy eigenstates ϵ_n and fulfills the normalization[2]:
$\sum_k \omega_n(k) = 1$.
With SW approch, one can investigate the direct observation of the valence band ant crossing in $CsPb(I_{1-x}Br_x)_3$ which is difficult to identify in standard band structure calculations [2]. By adding a small fraction of bromide (25% to 100%) in the host $CsPbI_3$ perovskite, results in a drastic increasing of their energy gap [2]. This wide band gap is

attributed to an anticrossing between the states of the host conduction band and the bromide states.

Reference

[1] https://github.com/rubel75/fold2Bloch-Wien2k/wiki/fold2Bloch-Guide

[2] Rubel, O.; Bokhanchuk, A.; Ahmed, S.J.; Assmann, E. Unfolding the band structure of disordered solids: From bound states to high-mobility Kane fermions. Phys. Rev. B - Condens. Matter Mater. Phys. 2014, 90, 115202.