Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information: Influence of A Site Cation on Nonlinear Band Gap Dependence of 2D Ruddlesden-Popper $A_2Pb_{1-x}Sn_xI_4$ Perovskites

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Other Materials

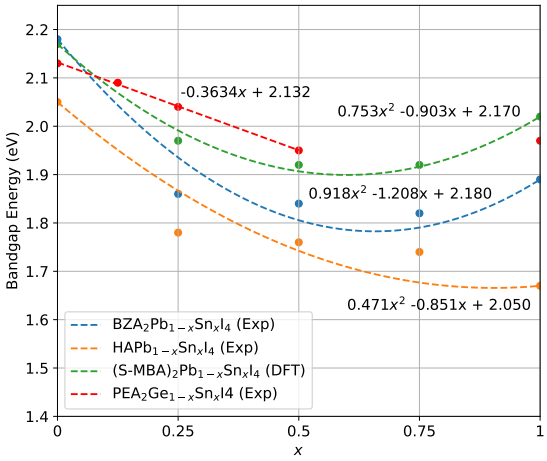
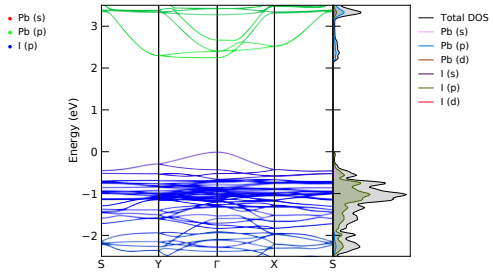
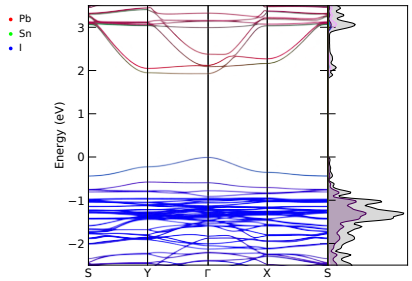


Figure S1: Reported band gaps of different 2D RPPs solid solutions, where BZA = benzylammonium, HA = histammonium, S-MBA = the s orientation of chiral methylbenzylammonium and PEA = phenethylammonium. The x axis shows Sn content and the y axis shows the band gap of the structure measured from optical absorption spectroscopy or calculated using DFT. The dotted line shows a non-linear or linear fit to each dataset. ? ? ? ?

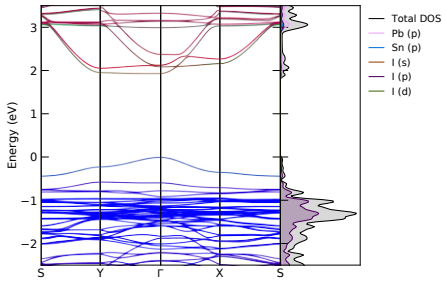
Electronic Band Structures



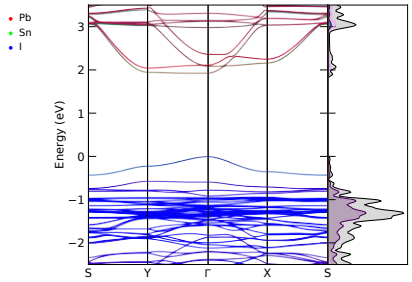
(a) MA_2PbI_4



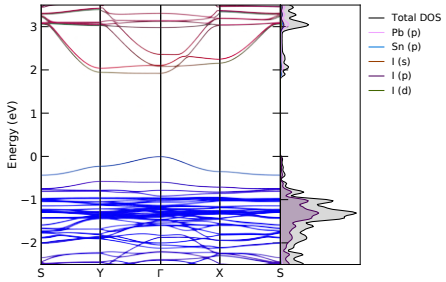
(b) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 1



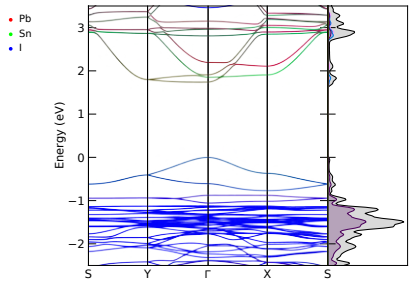
(c) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 2



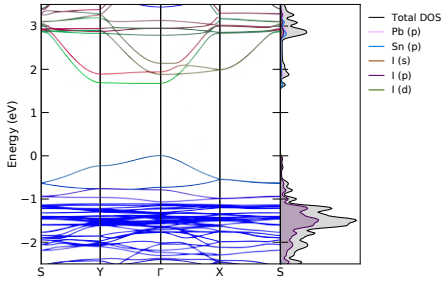
(d) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 3



(e) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 4



$MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 1



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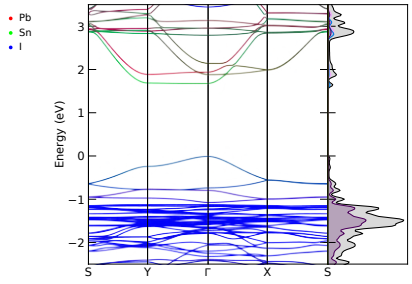
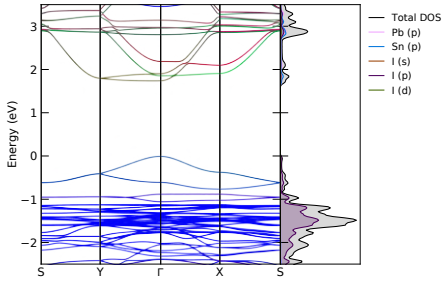


(h) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 3



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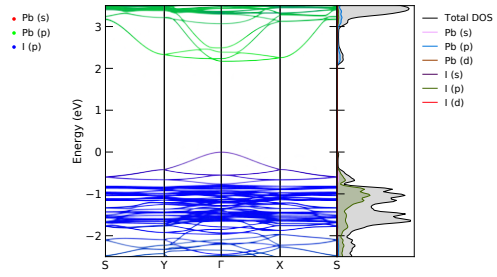
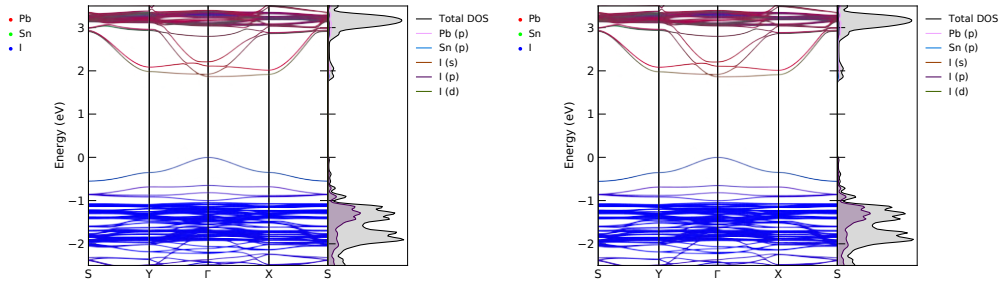
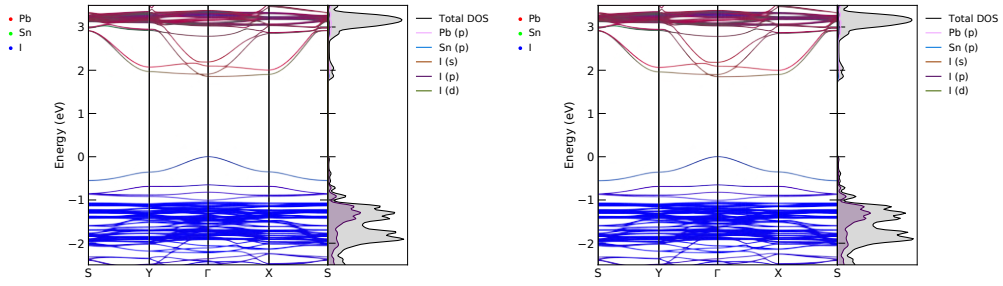


(a) PEA_2PbI_4



(b) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 1

(c) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 2



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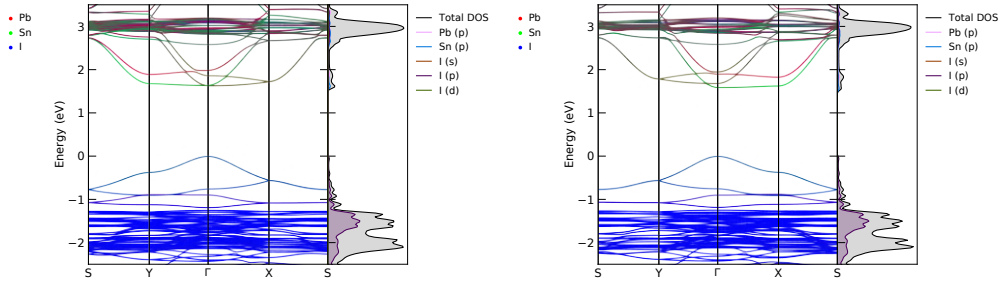
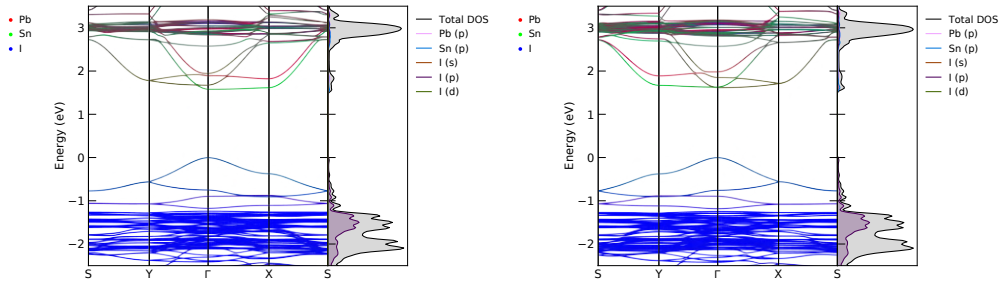
(e) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 4



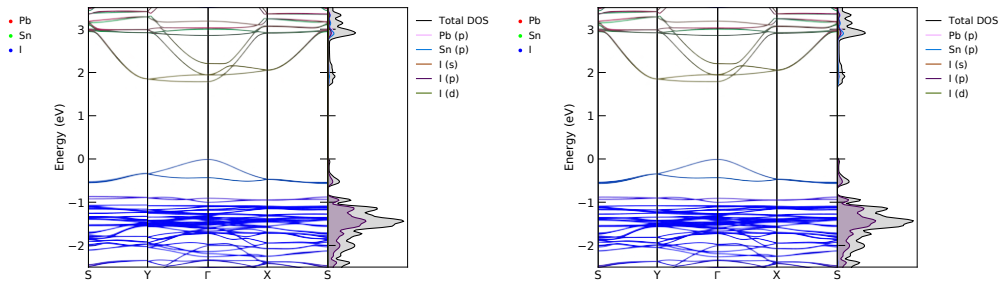
(f) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 1

(g) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 2

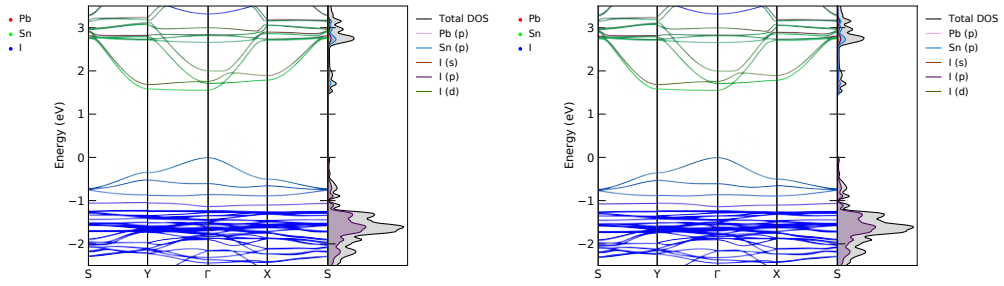


(h) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 3

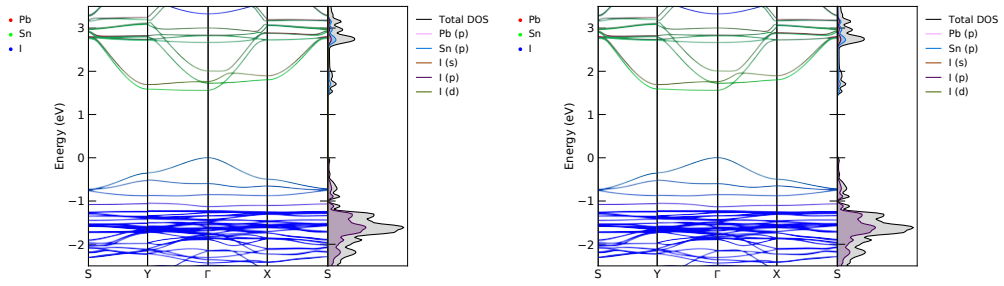
(i) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 4



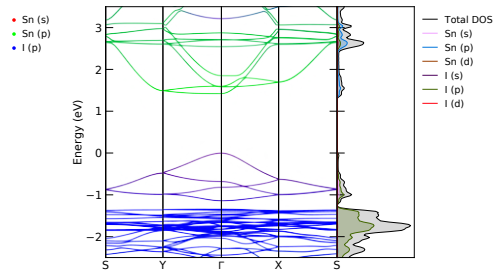
(j) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 1 (k) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 2



(l) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 1 (m) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 2

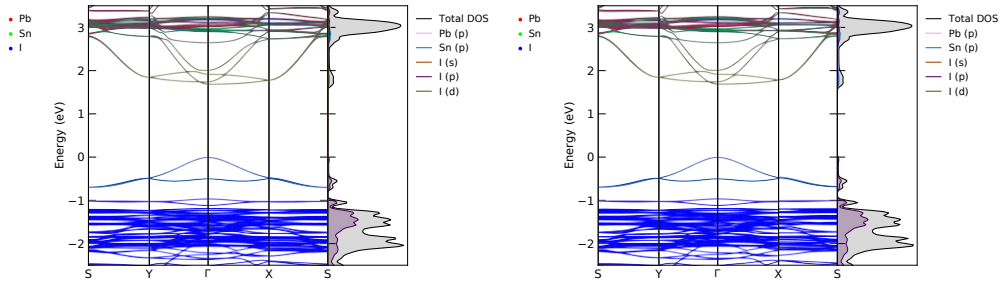


(n) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 3 (o) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 4

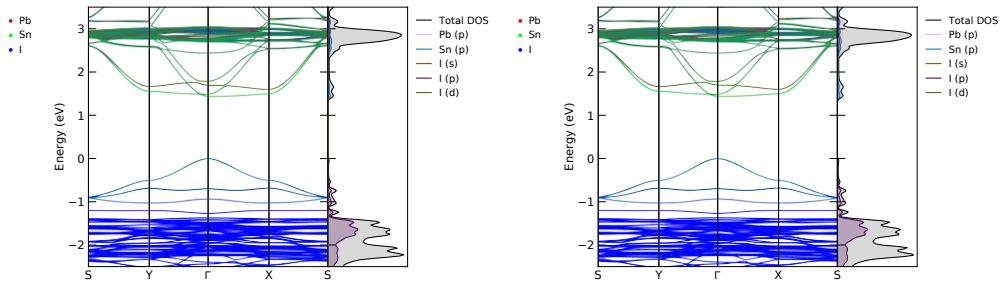


(p) MA_2SnI_4

Figure S2: Band structure and density of states plots for the 16 permutations of $MA_2Pb_{1-x}Sn_xI_4$ with increasing Sn content. The key in the top left of each graph describes the colour of each band structure plot, and the key in the top right refers to the density of states plot.



(j) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 1 (k) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 2



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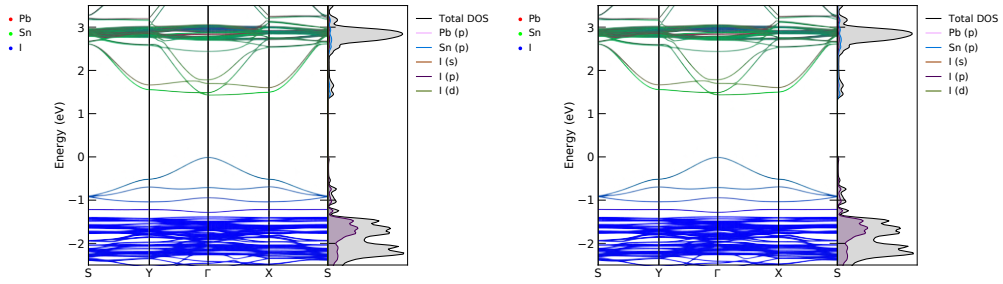

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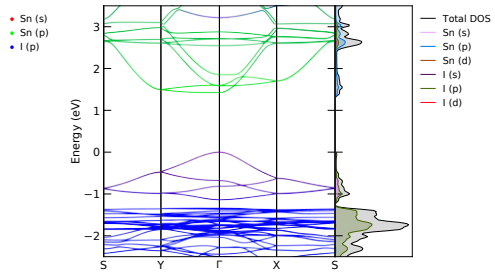
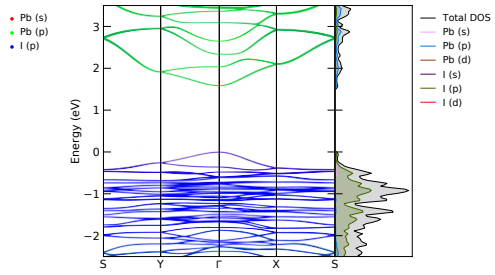
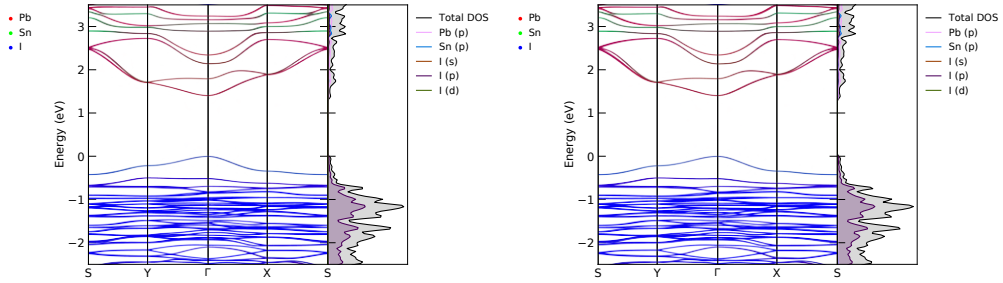


(p) PEA_2SnI_4

Figure S3: Band structure and density of states plots for the 16 permutations of $PEA_2Pb_{1-x}Sn_xI_4$ with increasing Sn content. The key in the top left of each graph describes the colour of each band structure plot, and the key in the top right refers to the density of states plot.

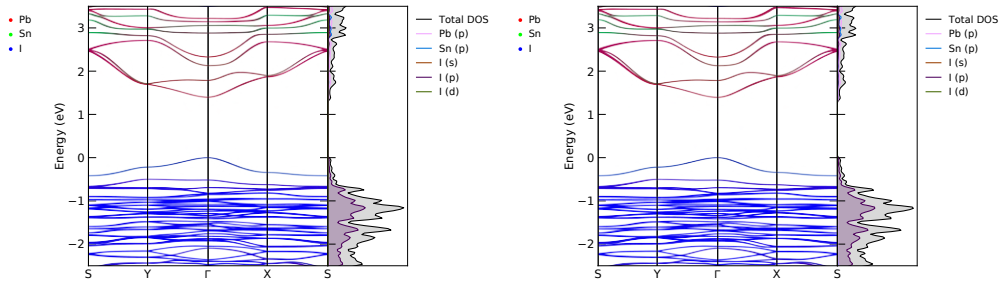


(a) MA_2PbI_4



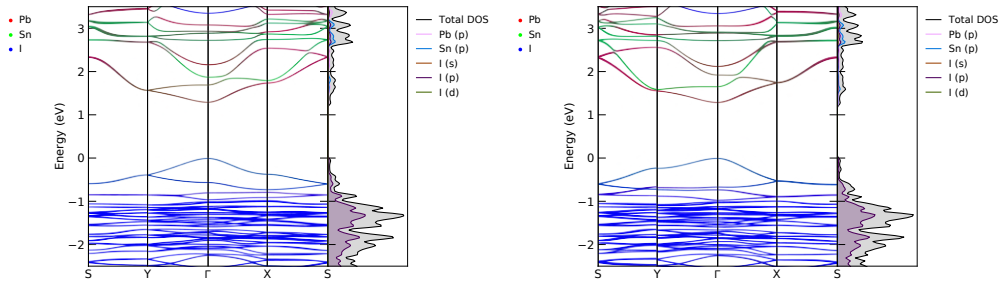
(b) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 1

(c) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 2



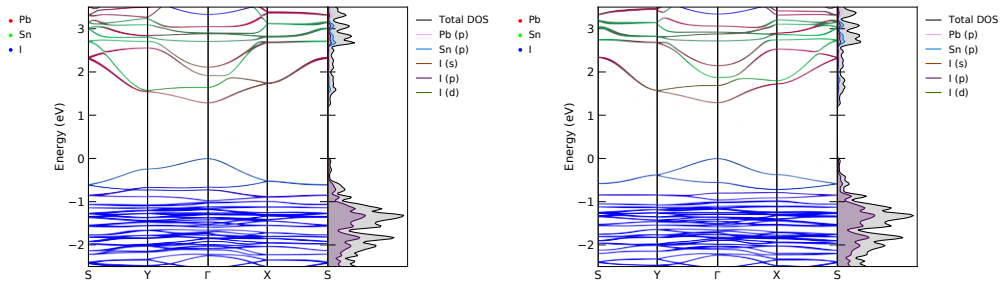
(d) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 3

(e) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 4



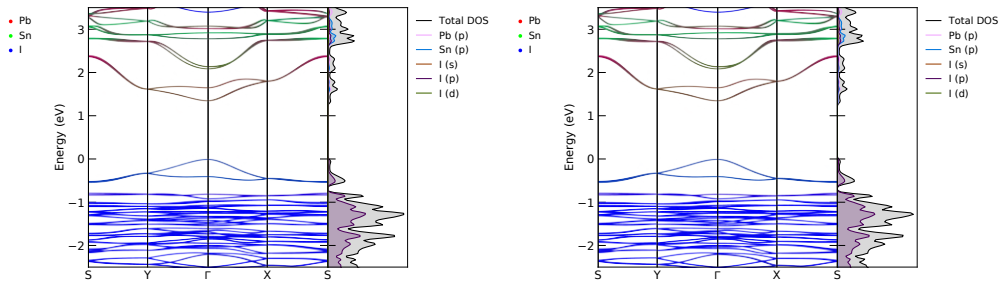
(f) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 1

(g) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 2

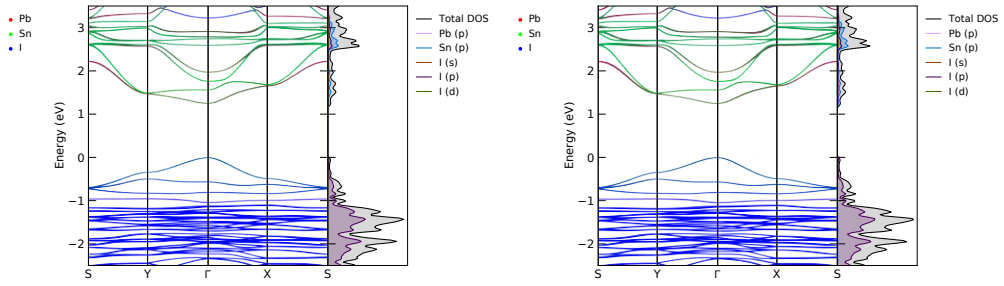


(h) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 3

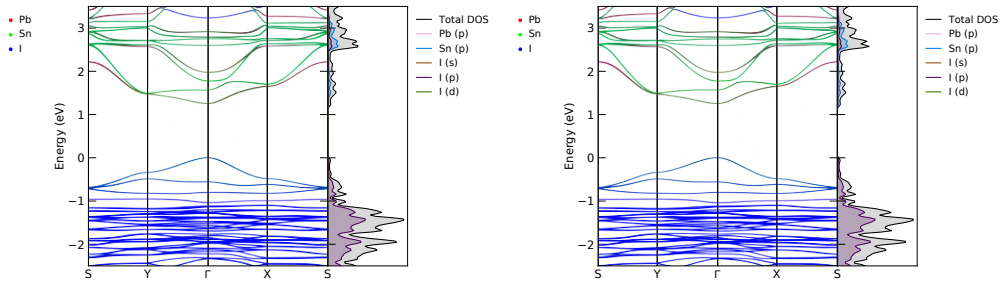
(i) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 4



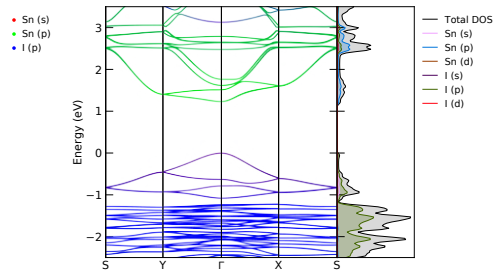
(j) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 1 (k) $MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 2



(l) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 1 (m) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 2

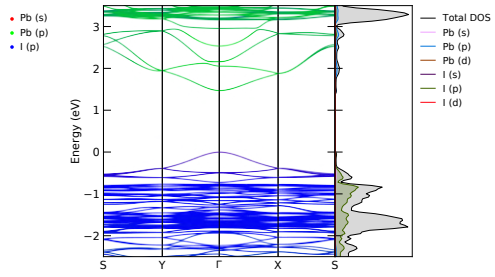


(n) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 3 (o) $MA_2Pb_{0.75}Sn_{0.25}I_4$ 4

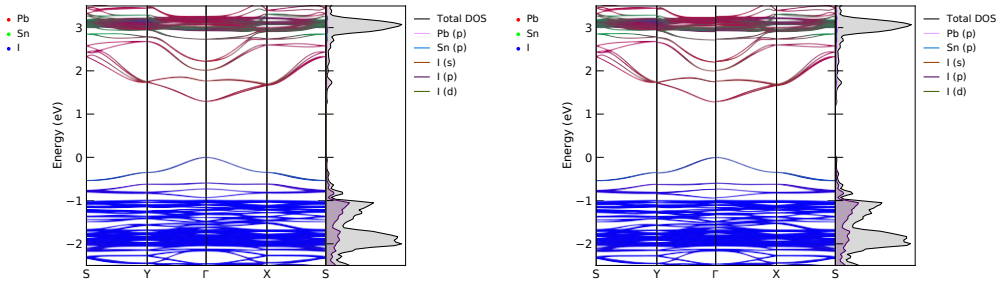


(p) MA_2SnI_4

Figure S4: Band structure and density of states plots with SoC for the 16 permutations of $MA_2Pb_{1-x}Sn_xI_4$ with increasing Sn content. The key in the top left of each graph describes the colour of each band structure plot, and the key in the top right refers to the density of states plot.

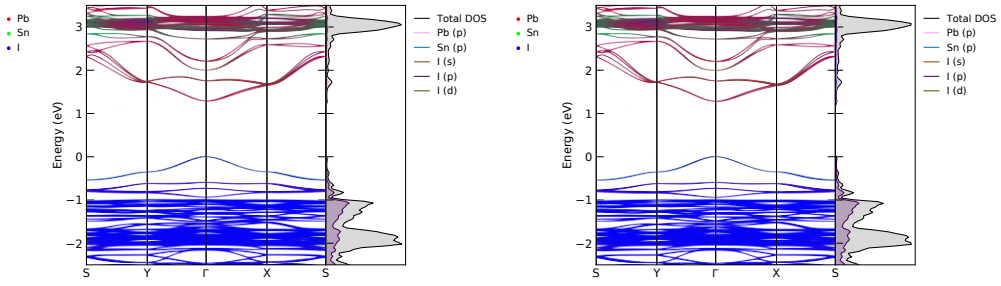


(a) PEA_2PbI_4



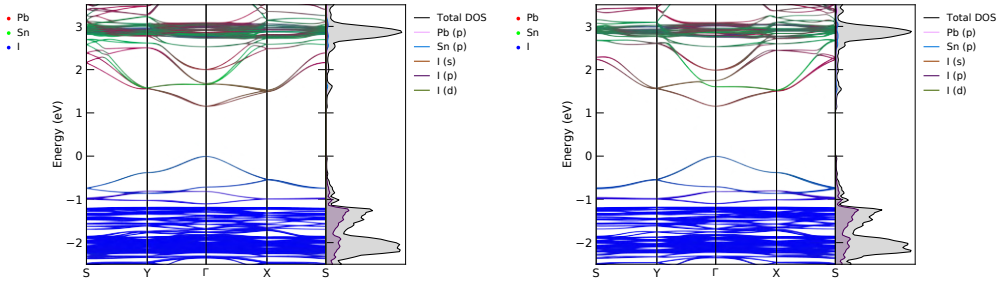
(b) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 1

(c) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 2



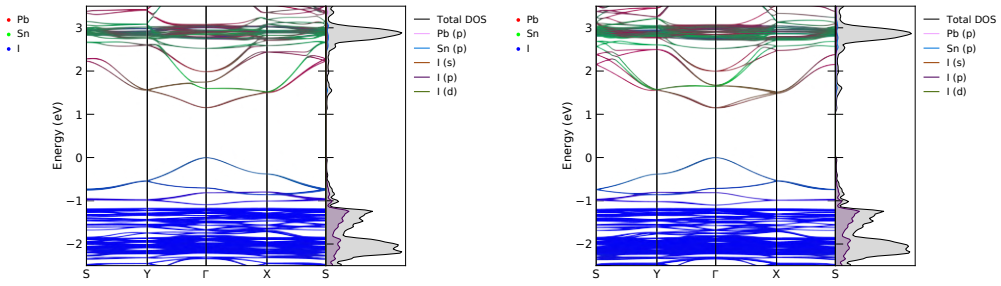
(d) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 3

(e) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 4



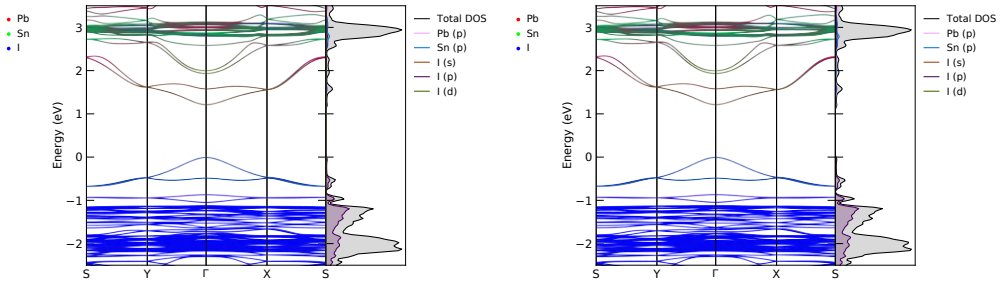
(f) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 1

(g) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 2

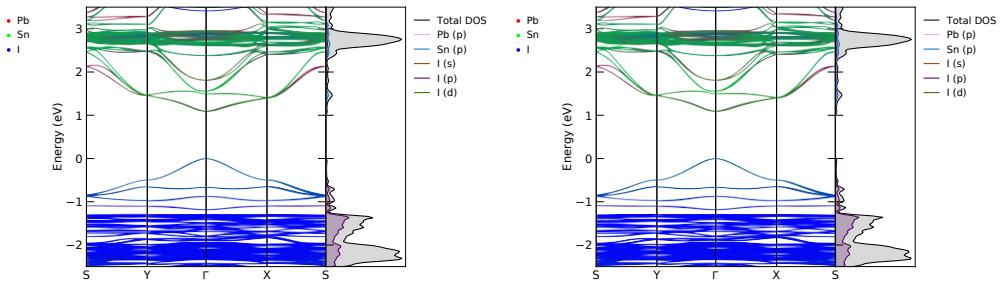


(h) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 3

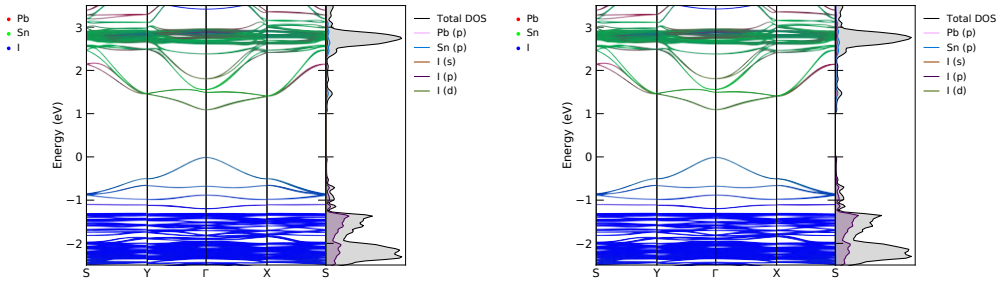
(i) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' 4



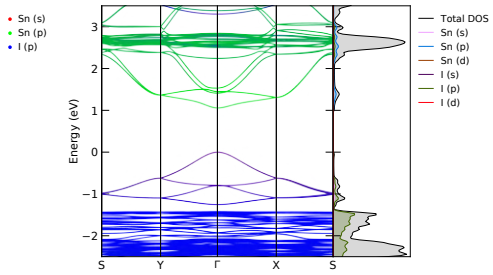
(j) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 1 (k) $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg' 2



(l) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 1 (m) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 2



(n) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 3 (o) $PEA_2Pb_{0.75}Sn_{0.25}I_4$ 4



(p) PEA_2SnI_4

Figure S5: Band structure and density of states plots for the 16 permutations of $PEA_2Pb_{1-x}Sn_xI_4$ with increasing Sn content. The key in the top left of each graph describes the colour of each band structure plot, and the key in the top right refers to the density of states plot.

Band Gap of $A_2Pb_{1-x}Sn_xI_4$

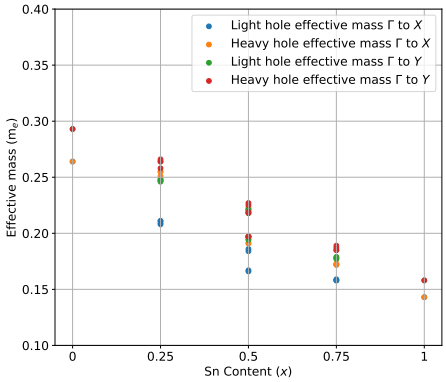
Table S1: Band gaps of $MA_2Pb_{1-x}Sn_xI_4$ based on different permutations. The band gap decreases with increasing Sn content when using SoC or not. The is significant in $MA_2Pb_{0.5}Sn_{0.5}I_4$, especially when SoC is not used. The effect of SoC is more significant in Pb heavy solid solutions, due to the higher quantum numbers in the Pb electronic configuration compared to Sn.

Configuration	**Bandgap without SoC**			
MA_2PbI_4	2.243 eV			
$MA_2Pb_{0.75}Sn_{0.25}I_4$	1.923 eV	1.926 eV	1.926 eV	1.924 eV
$MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns'	1.726 eV	1.670 eV	1.671 eV	1.733 eV
$MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg'	1.782 eV		1.785 eV	
$MA_2Pb_{0.75}Sn_{0.25}I_4$	1.559 eV	1.557 eV	1.555 eV	1.558 eV
MA_2SnI_4	1.415 eV			
Configuration	**Bandgap with SoC**			
MA_2PbI_4	1.578 eV			
$MA_2Pb_{0.75}Sn_{0.25}I_4$	1.395 eV	1.395 eV	1.394 eV	1.391 eV
$MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns'	1.287 eV	1.283 eV	1.285 eV	1.290 eV
$MA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg'	1.345 eV		1.346 eV	
$MA_2Pb_{0.75}Sn_{0.25}I_4$	1.251 eV	1.249 eV	1.247 eV	1.247 eV
MA_2SnI_4	1.225 eV			

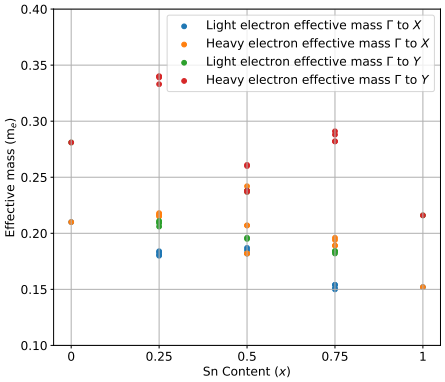
Table S2: Band gaps of $PEA_2Pb_{1-x}Sn_xI_4$ based on different permutations. The band gap decreases with increasing Sn content when using SoC or not. The is significant in $PEA_2Pb_{0.5}Sn_{0.5}I_4$ for the same reasons described for $MA_2Pb_{0.5}Sn_{0.5}I_4$.

Configuration	**Bandgap without SoC**			
PEA_2PbI_4	2.162 eV			
$PEA_2Pb_{0.75}Sn_{0.25}I_4$	1.855 eV	1.850 eV	1.848 eV	1.843 eV
$PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns'	1.619 eV	1.579 eV	1.580 eV	1.617 eV
$PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg'	1.677 eV		1.680 eV	
$PEA_2Pb_{0.75}Sn_{0.25}I_4$	1.437 eV	1.435 eV	1.431 eV	1.436 eV
PEA_2SnI_4	1.271 eV			
Configuration	**Bandgap with SoC**			
PEA_2PbI_4	1.462 eV			
$PEA_2Pb_{0.75}Sn_{0.25}I_4$	1.286 eV	1.283 eV	1.281 eV	1.274 eV
$PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns'	1.147 eV	1.149 eV	1.151 eV	1.148 eV
$PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Battenberg'	1.207 eV		1.210 eV	
$PEA_2Pb_{0.75}Sn_{0.25}I_4$	1.093 eV	1.093 eV	1.089	1.092 eV
PEA_2SnI_4	1.047 eV			

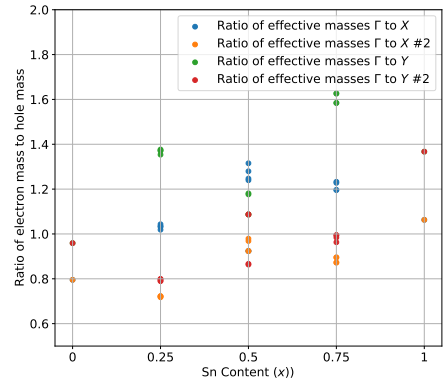
Effective Masses



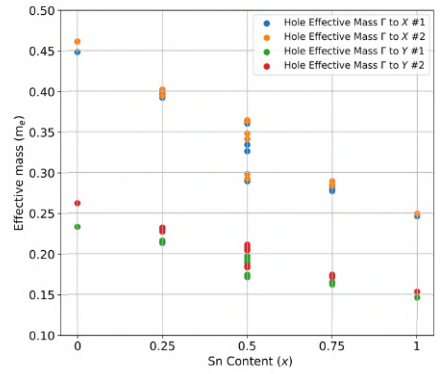
(a) Effective hole masses for $PEA_2Pb_{1-x}Sn_xI_4$.



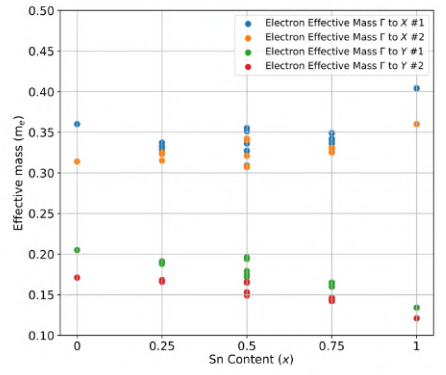
(b) Effective electron masses for $PEA_2Pb_{1-x}Sn_xI_4$.



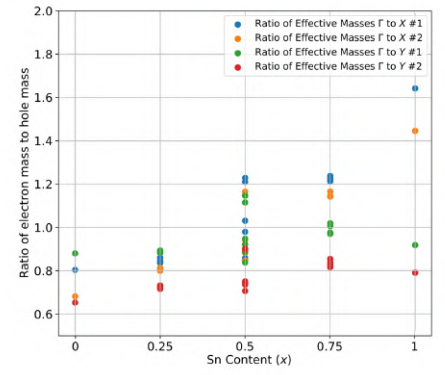
(c) Ratio of effective hole and electron Masses for $PEA_2Pb_{1-x}Sn_xI_4$.



(a) Effective hole masses for $MA_2Pb_{1-x}Sn_xI_4$.



(b) Effective electron masses for $MA_2Pb_{1-x}Sn_xI_4$.



(c) Ratio of effective hole and electron masses for $MA_2Pb_{1-x}Sn_xI_4$.

Figure S6: Effective Hole and Electron masses for $PEA_2Pb_{1-x}Sn_xI_4$ and $MA_2Pb_{1-x}Sn_xI_4$. A decreasing trend in effective mass for increasing Sn content is shown. The ratio of hole and electron effective masses is closest to 1 in the case of $x = 0.5$, where both effective masses are 0.2 m_0.

Input Structures

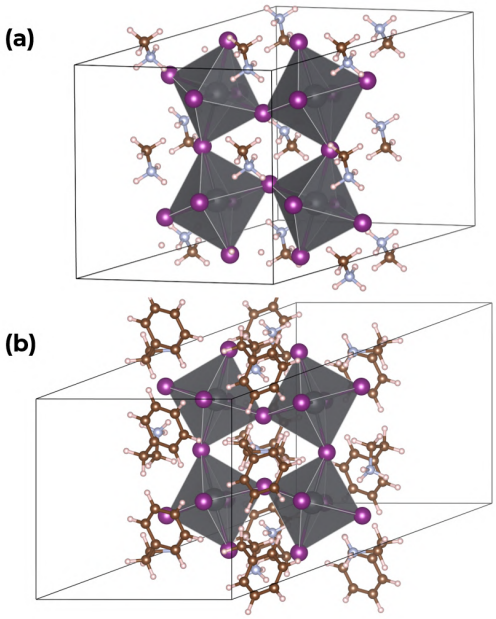


Figure S7: Initial unit cell of (a) MA_2PbI_4 and PEA_2PbI_4 from Gebhardt *et al.*[?] Initial inputs are generated for various Pb-Sn permutations and fully relaxed in VASP.

CBM Without SoC

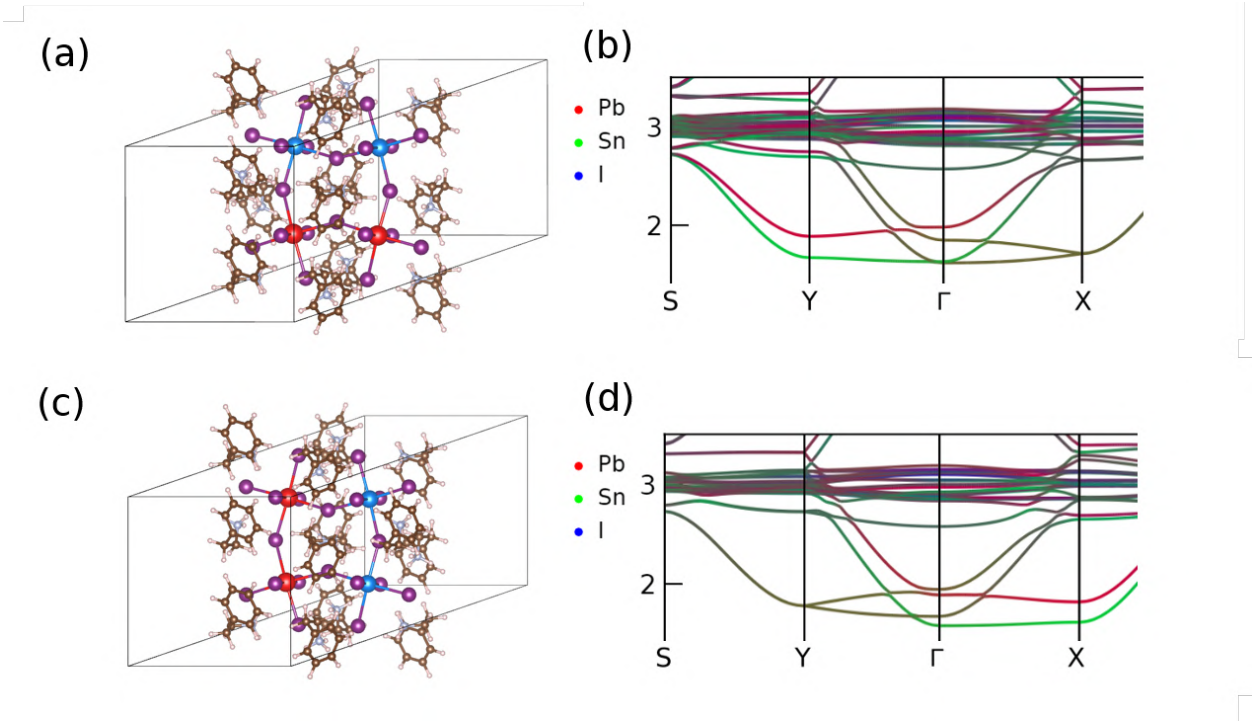


Figure S8: $PEA_2Pb_{0.5}Sn_{0.5}I_4$ 'Columns' Permutations 1 and 4, of bandgap 1.619 eV and 1.580 eV respectively. 1 show the pairs of Pb and Sn atoms along the in-flexed x axis, and 2 show pairs of Pb and Sn atoms along the out-flexed b axis. Pb is shown in red, and Sn is shown in blue in position files.