Nonlinear Band Gap Dependence of Mixed Pb-Sn 2D Ruddlesden-Popper $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ Perovskites

Cameron Underwood, J. David Carey, and S. Ravi P. Silva*

*Advanced Technology Institute, Department of Electrical & Electronic Engineering,
University of Surrey, Guildford, GU2 7XH, U.K*

E-mail: s.silva@surrey.ac.uk

Abstract

Two dimensional (2D) Ruddlesden-Popper perovskites (RPPs) of the form $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ can be used as the tunable active layer in photovoltaics, as the passivating layer for 3D perovskite photovoltaics or in light emitting diodes. Here we show a nonlinear band gap behaviour with Sn content in mixed phase 2D RPPs. Density functional theory calculations (with and without spin-orbit coupling) are employed to study the effects of the short range ordering of Pb and Sn in $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ compositions with $x = 0, 0.25, 0.5, 0.75$ and 1. Analysis of the partial density of states shows the energy mismatch of the Pb 6s and Sn 5s states in the valence band maximum determines the nonlinearity of the band gap, leading to a bowing parameter of 0.35 - 0.38 eV. This research provides a critical insight for the design of future metal alloy 2D perovskite materials. The positions of the tunable energy band discontinuity may point to intra-band transitions of interest to device engineers.

Hybrid organic inorganic perovskites (HOIP) have shown significant potential as the absorber layer within high performance photovoltaic (PV) devices with a relatively low fabrication cost in the current PV market.^{1–4} Power conversion efficiencies (PCE) of HOIPs have made extremely rapid progress, increasing from 3.8% in 2009¹ to 25.5%.⁵ The vast majority of perovskite PVs use Pb as the metallic component of the absorber layer, although Sn has emerged as a strong contender to alloy with Pb to provide a degree of band gap tunability, or to replace Pb entirely to eliminate toxic by-products. A key issue with Sn and mixed Pb-Sn bulk 3D perovskites is device stability associated with the oxidation of Sn from the Sn²⁺ to the Sn⁴⁺ state; this reduces absorption efficiency and decreases the diffusion length causing a detrimental effect on device performance.^{6,7} One method to tune the band gap, whilst removing some unwanted Pb from devices, is in mixed Pb-Sn solution solutions. Mixed Pb-Sn 3D perovskites have shown great success as individual active layers, as well as the bottom cell in a tandem configuration. By varying the ratio of Pb to Sn in these mixed Pb-Sn perovskites, the band gap can be tuned from 1.15-1.6 eV, with improved charge carrier properties relative to pure-Pb perovskites, and better stability relative to pure-Sn perovskites.^{8–10} Although, due to the stability limitations of Sn in 3D bulk perovskites, device performance is still limited, with PCEs currently exceeding 21%, approximately 4% less than the current record for pure-Pb.¹¹

Ruddlesden-Popper phase (RPP) perovskites have the general form $A_{1-n}A_2B_nX_{3n+1}$. The reduced dimensionality and structural characteristics of RPPs reportedly improve the stability of these crystals in comparison to their 3D counterparts.¹² When n is reduced to 1, the general formula becomes A_2BX_4 , the reduced dimensionality and structural composition of this 2D configuration improves the stability of the crystal compared to their 3D counterparts as the large organic A site cation effectively passivates dangling ionic bonds. This reduces the number of pathways for oxygen and water adsorption into the lattice which prevents decay into toxic byproducts. Sn is particularly well suited for alloying with Pb due to their similar ionic radii, 1.19 Å for Pb²⁺ and 1.18 Å for Sn²⁺,¹³ as well as similar electronic

configuration resulting in compatible structures and semiconducting behaviour. 2D RPPs generally have a larger band gap than 3D perovskites due to the decrease in dimensionality. As the dimensionality decreases from 3D to 2D, the connectivity of the octahedra along one dimension is broken, resulting in less band dispersion for both the valence band maximum (VBM) and conduction band minimum (CBM); this causes an increased band gap.^{14,15}

Due to the larger band gap and increased stability of 2D RPPs, they can also be used as a surface passivation layer for 3D perovskites, which can decrease unwanted oxidation or ion migration. This was shown by Zeng *et al.* for a mixed Pb-Sn system, reducing unwanted recombination in the 3D bulk perovskite, increasing the PCE of the device from around 12.5% to around 15%.¹⁶ Li *et al.* also showed that the phenethylammonium (PEA) molecule can be used to passivate trap states due to I^- and FA^+ vacancies on the surface.¹⁷ Furthermore, due to the reduced dimensionality, the exciton binding energy increases and the band gap blue shifts which is useful for colour selective light emitting diode (LED) applications.¹⁸

Alloying the B site of a 3D perovskite has been shown to allow for the design of low band gap perovskites, due to the significant band gap bowing in $MAPb_{1-x}Sn_xI_3$, with a band gap minima of 1.15 eV for $x = 0.5$.¹⁹ On the other hand, alloying of the B site of a 2D perovskite can lead to other unique properties, as demonstrated by Li *et al.* by incorporating a small amount of Sn in $PEA_2MA_{n-1}Pb_nI_{3n+1}$ which strongly intensified broadband emission in RPPs LEDs.²⁰ The effect on the band gap for Pb-Sn alloys also varies for each perovskite system, allowing for various band gap tunability, and appears dependant on the choice of A site. Lu *et al.* showed that for the chiral A site of methylbenzylammonium (R/S-MBA), the band gap dependence with increasing alloy was significantly nonlinear.²¹ Mao *et al.* showed nonlinearity for the A site of histammonium in Dion-Jacobson $HAPb_{1-x}Sn_xI_4$ and in benzylammonium in $BZA_2Pb_{1-x}Sn_xI_4$.²² Cheng *et al.* observed a linear behaviour of the band gap in the case of $PEA_2Ge_{1-x}Sn_xI_4$ between $x = 0$ and 0.5, with a higher band gap shown in $x = 1$, suggesting positive linearity between $x = 0.5$ and 1 or very significant nonlinearity in this region.²³

Here, we study the mixed B site, $n=1$ case, of the form $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ with and without spin-orbit coupling (SOC) and for different supercell permutations. Band structures and density of states (DOS) are calculated; the band gaps are compared as a function of B site composition, x , to explore the nonlinearity in each case and the partial density of states (PDOS) is calculated to show the origin of the VBM and CBM characteristics. We also discuss the impact of using SOC to understand the properties of the CBM behaviour as well as band gap dependence on short range ordering of Pb and Sn atoms. The bowing parameter, b , describes how nonlinear the band gap dependence is and is given by Equation 1.

$$E_g(x) = (1 - x)E_{g(x=0)} + xE_{g(x=1)} - bx(1 - x) \quad (1)$$

The origin of band gap bowing (b) can be a combination of (1) changes in bond angles/lengths, (2) chemical effects, such as differing CBM and VBM contributing orbital energies and (3) volume deformation potential effects, which are changes in the electronic structure of pure compounds due to the changes in the volume.^{14,19}

The structural and electronic properties for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ are calculated from first principles using non-collinear density functional theory (DFT) employing the Perdew-Berke-Ernerhof (PBE) generalized gradient approximation²⁴ implemented in the Vienna *ab initio* simulation program (VASP).^{25–28} Projector augmented-wave PBE pseudopotentials^{29,30} are used, with and without, the addition of spin-orbit coupling (SOC) to show the effects of SOC. Wave functions are expanded in the plane-wave basis up to an energy cutoff of 520 eV. Total energies are fully relaxed to 3×10^{-9} eV and atomic forces are relaxed to 0.01 Å/eV using a DFT-2 van der Waals correction for relaxation calculations, fixing the unit cell volume to avoid collapsing the vacuum along z , which is approximately 15 Å. These calculations are sampled with a $4 \times 4 \times 1$ gamma centered k-point grid. The resulting band structure and density of states were calculated using an initial DFT pre-convergence, a PBE energy calculation and a PBE band structure calculation using an energy convergence

criteria of 3×10^{-9} eV and an energy cutoff of 400 eV. The bandpath was autogenerated using SeekPath^{31,32} and takes the path of S - Y - Γ - X - S with a k-point spacing of 100 and is plotted using sumo-bandplot.³³ The structural analysis is completed using Atomic Simulations Environment (ASE)³⁴ and post-processed using Matplotlib, SciPy, Numpy and Seaborn.^{35–38} Band structure plot fitting was performed in Python with the use of SciPy and NumPy. Initial position inputs for PEA_2PbI_4 are taken from Gebhardt *et al.*³⁹ The simplified unit cell makes it an ideal environment for examining the effects of alloying the B site cation. For a generic $n=1$ RPP with a mixed B site of form $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ the permutations are shown in Figure 1 where B1 and B2 can occupy positions 1, 2, 3 and 4 in each of the four octahedra around the unit cell; the permutations are denoted by the label ‘Columns’ or ‘Battenberg’, depending on the short range ordering of Pb and Sn ions in the four B ion sites. All permutations are studied to interpret the behaviour of a large, anisotropic system.^{19,40}

Figure 1: Visualisation of the 16 permutations of $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ where $x = 0, 0.25, 0.5, 0.75$ and 1 , where Pb (red), Sn (blue) and I (purple) atoms are identified. When $x = 0.5$, we distinguish the difference between the short range ordering of Pb and Sn atoms with the labels ‘Columns’ and ‘Battenberg’.

All resultant band structures are direct at the Γ point and show no Rashba splitting, which is consistent with literature.^{39,41} The band gap (eV) as a function of Sn content (%) for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$, with and without SOC, is shown in Figure 2 and shows a bowing constant b of 0.379 eV and 0.352 eV for the calculation, with and without SOC, respectively. This indicates that SOC does not significantly affect the non-linearity of the system, but it is crucial in understanding the characteristics of the band edges.³⁹ The band gap behaviour for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ is nonlinear but is less pronounced than the bowing parameter of 1.08 eV in the case of 3D bulk $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$ as shown by Goyal *et al.*,¹⁹ and less pronounced than other

2D RPPs. Materials such as $\text{BZA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$, $\text{HAPb}_{1-x}\text{Sn}_x\text{I}_4$ and $(\text{S-MBA})_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ have previously been shown to have bowing parameters of 0.918 eV, 0.471 eV and 0.753 eV, respectively. The bowing parameters in $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ are similar, with and without SOC, but is relatively more pronounced in the case of SOC as the relative positions of $E_{g(x=0)}$ and $E_{g(x=1)}$ are much closer. The bowing parameter in $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ is dependant on the choice of permutation for $x = 0.5$; where the ‘Battenberg’ structure gives rise to a more linear band gap dependence due to the higher band gap, and the ‘Columns’ permutation give rise to a more nonlinear band gap dependence due to the lower band gap. The average of the six permutations for $x = 0.5$ gives rise to the fit shown in the Supplimentary Information. The difference in energy of both structures are less than 1 meV per atom, as shown in Figure S1, but the energy of the ‘Battenberg’ structure, is slightly larger than the energy of the ‘Columns’ structure by between 0.03 - 0.16 meV per atom depending on the permutation, which is comparable to halide permutations shown for $\text{Cs}_2\text{PbI}_2\text{Cl}_2$.^{42,43}

Figure 2: Variation of band gap (eV) as a function of Sn content (%) for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$, with and without SOC. The bowing parameter is 0.352 eV and 0.379 eV, respectively, with and without SOC. The linear term is -0.766 eV and -1.270 eV, respectively, this is due to SOC affecting Pb much more than Sn, due to the higher electronic configuration of Pb.

Structural relaxations cause a slight decrease in lattice parameters for increasing Sn content in a similar trend to $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$,¹⁹ due to the slightly smaller ionic radius of Sn^{2+} compared to Pb^{2+} . To understand the effect of the structural relaxation on calculated band gaps, an analysis of the lattice parameters, bond lengths and bond angles as a function of increasing Sn content and, for each permutation, is shown in Figure 3. A slight decrease in the a and b lattice parameters is shown in Figure 3(a) with increasing Sn content; this can be attributed to the slightly smaller ionic radius of Sn^{2+} compared to Pb^{2+} , as well as the smaller Sn-I bond length compared to Pb-I as shown in in Figure 3(b). This bond length does not change significantly as a function of increasing Sn content or decreasing

lattice parameters, so can be attributed directly to the interaction between Pb and I atoms or between Sn and I atoms, respectively, and explains the relative lattice parameter decrease. An increase of opposite in-plane X-B-X bond angles is shown with increasing Sn content as shown in Figure 3(c). The positive gradient of both X-B-X bond angles is similar but the y intercept is different, which is likely attributed to the lower atomic mass of Sn compared with Pb where in this case the I-Pb-I bond angles are lower than the I-Sn-I bond angles along the plane where Pb and Sn atoms repeat. The Sn-I-Sn bond angles are also consistently larger than the Pb-I-Pb bond angles as shown in Figure 3(d), suggesting less octahedral tilting. An increase of the B-X-B angle increases the overlap of the B-X antibonding orbitals, thus increasing the VBM energy and reducing the band gap.⁴⁴

Figure 3: Structural analysis showing (a) a and b lattice parameters, (b) Pb-I and Sn-I bond lengths, (c) opposite I-Pb-I and I-Sn-I bond angles and (d) Pb-I-Pb and Sn-I-Sn angles as function of Sn constant showing various permutations. A line of best fit is shown with a confidence interval supplied by seaborn,³⁸ shown by the shaded area. For the Pb-I-Pb and Sn-I-Sn bond angles at $x = 0.5$, the difference is when the Sn atoms are along the a or b direction, flexing in or out of the unit cell.

The results shown in Figure 4 show VBM characteristics similar to that shown in the VBM and CBM of 3D $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$ demonstrated by Goyal *et al.*¹⁹. In mixed Pb-Sn permutations, the Sn 5s - I 5p anti-bonding states are shown to occupy higher energies in the VBM as compared to the Pb 6s - I 5p anti-bonding states. This increased VBM due to Sn is described as part of the mechanism for intensifying broadband emission in RPPs LEDs.²⁰ This increased Sn VBM energy may be due to the electrons in Sn 5s being less attracted by their nuclei compared to Pb 6s, and therefore a shallower energy level, where Pb 6s = -11.6 eV and Sn 5s = -10.1 eV relative the vacuum.⁴⁵ As discussed earlier, this may also be contributed by the consistently higher Sn-I-Sn angles relative to the Pb-I-Pb angles, increasing the orbital overlap in the valence band minimum and decreasing the band gap, as shown in the partial density of states analysis. However, in the CBM, the Pb 6p states overlap with the Sn 5p DOS more evenly.

Figure 4: Variation of DOS highlighting the VBM and CBM composition for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ with SOC. The VBM consists mostly of I 5p, Sn 5s and Pb 6s, whereas the CBM consists mostly of Pb 6p and Sn 5p. The Sn 5s states occupy higher energy than the Pb 6s states in the VBM, contributing to the decrease in band gap.

The nonlinear dependence of the band gap in $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$ was studied using DFT calculations and showed a nonlinear band gap dependence with a band gap bowing of 0.352 eV, significantly less than 1.08 eV calculated for $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$ 3D perovskites.¹⁹ The origins of the nonlinearity are shown to be due to the chemical behaviour of the relative energies of the Sn 5s and Pb 6s states in the VBM composition. This is also influenced by the increased I-Sn-I angles relative to I-Pb-I angles, the increased angles result in a higher overlap between I and Sn orbitals, resulting in a higher dispersion and a decreased band gap. The short range ordering of Pb and Sn atoms is discussed, especially in the case of $x = 0.5$, where the short range ordering is most significant, the band gap energy is shown to be dependant on this. We have also highlighted the role of using SOC in calculations of 2D RPPs, discussing that SOC does not significantly affect the nonlinearity of the band gap, but strongly affects the linear term, and is also crucial for understanding other electronic properties of 2D RPPs. This research underlines the importance of supercell permutations as well as providing a good platform to study other 2D perovskites, such as other A sites, other mixed B sites, or mixed halide RPPs.

Acknowledgement

This work was funded and supported by the Engineering and Physical Sciences Research Council (EPSRC) Grant Number GR/1922310/1. The authors would like to thank Joshua Reding for very useful discussions and proof reading about the theoretical concepts throughout the paper.

Supporting Information Available: Comparison of total energy for $\text{PEA}_2\text{Pb}_{1-x}\text{Sn}_x\text{I}_4$, comparing short range ordering, Figure S1.

References

- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society* **2009**, *131*, 6050–6051.
- (2) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **2013**, *499*, 316.
- (3) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The emergence of perovskite solar cells. *Nat. Photonics* **2014**, *8*, 506.
- (4) Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **2013**, *501*, 395.
- (5) NREL, Best Research-Cell Efficiencies. 2020.
- (6) Bandara, R.; Jayawardena, K.; Adeyemo, S.; Hinder, S.; Smith, J.; Thirimanne, H.; Wong, N.; Amin, F.; Freestone, B.; Parnell, A., et al. Tin (iv) dopant removal through anti-solvent engineering enabling tin based perovskite solar cells with high charge carrier mobilities. *J. Mater. Chem. C* **2019**, *7*, 8389–8397.
- (7) Leijtens, T.; Prasanna, R.; Gold-Parker, A.; Toney, M. F.; McGehee, M. D. Mechanism of tin oxidation and stabilization by lead substitution in tin halide perovskites. *ACS Energy Lett.* **2017**, *2*, 2159–2165.
- (8) Eperon, G. E.; Leijtens, T.; Bush, K. A.; Prasanna, R.; Green, T.; Wang, J. T.-W.; McMeekin, D. P.; Volonakis, G.; Milot, R. L.; May, R., et al. Perovskite-perovskite tandem photovoltaics with optimized band gaps. *Science* **2016**, *354*, 861–865.
- (9) Zhao, B.; Abdi-Jalebi, M.; Tabachnyk, M.; Glass, H.; Kamboj, V. S.; Nie, W.; Pearson, A. J.; Puttison, Y.; Gödel, K. C.; Beere, H. E., et al. High Open-Circuit Voltages

- in Tin-Rich Low-Bandgap Perovskite-Based Planar Heterojunction Photovoltaics. *Adv. Mater.* **2017**, *29*, 1604744.
- (10) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* **2013**, *52*, 9019–9038.
- (11) Xiao, K.; Lin, R.; Han, Q.; Hou, Y.; Qin, Z.; Nguyen, H. T.; Wen, J.; Wei, M.; Yeddu, V.; Saidaminov, M. I., et al. All-perovskite tandem solar cells with 24.2% certified efficiency and area over 1 cm² using surface-anchoring zwitterionic antioxidant. *Nature Energy* **2020**, *5*, 870–880.
- (12) Spanopoulos, I.; Hadar, I.; Ke, W.; Tu, Q.; Chen, M.; Tsai, H.; He, Y.; Shekhawat, G.; Dravid, V. P.; Wasielewski, M. R., et al. Uniaxial Expansion of the 2D Ruddlesden–Popper Perovskite Family for Improved Environmental Stability. *Journal of the American Chemical Society* **2019**, *141*, 5518–5534.
- (13) Zhou, Y.; Zhao, Y. Chemical stability and instability of inorganic halide perovskites. *Energy Environ. Sci.* **2019**, *12*, 1495–1511.
- (14) Xiao, Z.; Zhou, Y.; Hosono, H.; Kamiya, T.; Padture, N. P. Bandgap optimization of perovskite semiconductors for photovoltaic applications. *Chem. - Eur. J.* **2018**, *24*, 2305–2316.
- (15) Xiao, Z.; Meng, W.; Wang, J.; Mitzi, D. B.; Yan, Y. Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality. *Mater. Horiz.* **2017**, *4*, 206–216.
- (16) Zeng, L.; Chen, Z.; Qiu, S.; Hu, J.; Li, C.; Liu, X.; Liang, G.; Brabec, C. J.; Mai, Y.; Guo, F. 2D-3D heterostructure enables scalable coating of efficient low-bandgap Sn-Pb mixed perovskite solar cells. *Nano Energy* **2019**, *66*, 104099.

- (17) Li, B.; Xiang, Y.; Jayawardena, K. I.; Luo, D.; Wang, Z.; Yang, X.; Watts, J. F.; Hinder, S.; Sajjad, M. T.; Webb, T., et al. Reduced bilateral recombination by functional molecular interface engineering for efficient inverted perovskite solar cells. *Nano Energy* **2020**, 105249.
- (18) Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A. Electronic structures of lead iodide based low-dimensional crystals. *Phys. Rev. B* **2003**, 67, 155405.
- (19) Goyal, A.; McKechnie, S.; Pashov, D.; Tumas, W.; Van Schilfgaarde, M.; Stevanovic, V. Origin of Pronounced Nonlinear Band Gap Behavior in Lead–Tin Hybrid Perovskite Alloys. *Chem. Mater.* **2018**, 30, 3920–3928.
- (20) Li, T.; Chen, X.; Wang, X.; Lu, H.; Yan, Y.; Beard, M. C.; Mitzi, D. B. Origin of Broad-Band Emission and Impact of Structural Dimensionality in Tin-Alloyed Ruddlesden–Popper Hybrid Lead Iodide Perovskites. *ACS Energy Lett.* **2019**, 5, 347–352.
- (21) Lu, H.; Xiao, C.; Song, R.; Li, T.; Maughan, A. E.; Levin, A.; Brunecky, R.; Berry, J. J.; Mitzi, D. B.; Blum, V., et al. Highly distorted chiral two-dimensional tin iodide perovskites for spin polarized charge transport. *Journal of the American Chemical Society* **2020**, 142, 13030–13040.
- (22) Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D., et al. Role of organic counterion in lead-and tin-based two-dimensional semiconducting iodide perovskites and application in planar solar cells. *Chem. Mater.* **2016**, 28, 7781–7792.
- (23) Cheng, P.; Wu, T.; Liu, J.; Deng, W.-Q.; Han, K. Lead-free, two-dimensional mixed Germanium and Tin perovskites. *J. Phys. Chem. Lett.* **2018**, 9, 2518–2522.
- (24) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, 3865.

- (25) Kresse, G.; Hafner, J. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558.
- (26) Kresse, G.; Hafner, J. *Ab initio* molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, *49*, 14251.
- (27) Kresse, G.; Furthmüller, J. Efficiency of *Abinitio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mat. Sci* **1996**, *6*, 15.
- (28) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Comput. Mat. Sci* **1996**, *54*, 11169.
- (29) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.
- (30) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.
- (31) Togo, A.; Tanaka, I. Spglib: a software library for crystal symmetry search. *arXiv preprint arXiv:1808.01590* **2018**,
- (32) Hinuma, Y.; Pizzi, G.; Kumagai, Y.; Oba, F.; Tanaka, I. Band structure diagram paths based on crystallography. *Comput. Mater. Sci.* **2017**, *128*, 140–184.
- (33) Ganose, A. M.; Jackson, A. J.; Scanlon, D. O. sumo: Command-line tools for plotting and analysis of periodic ab initio calculations. *Journal of Open Source Software* **2018**, *3*, 717.
- (34) Larsen, A. H. et al. The atomic simulation environment—a Python library for working with atoms. *J. Phys.: Condens. Matter* **2017**, *29*, 273002.
- (35) Hunter, J. D. Matplotlib: A 2D graphics environment. *Comput. Sci. Eng.* **2007**, *9*, 90–95.

- (36) Virtanen, P. et al. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nat. Methods* **2020**, *17*, 261–272.
- (37) Harris, C. R. et al. Array programming with NumPy. *Nature* **2020**, *585*, 357–362.
- (38) Waskom, M.; the seaborn development team, mwaskom/seaborn. 2020; DOI:10.5281/zenodo.592845.
- (39) Gebhardt, J.; Kim, Y.; Rappe, A. M. Influence of the Dimensionality and Organic Cation on Crystal and Electronic Structure of Organometallic Halide Perovskites. *The J. Phys. Chem. C* **2017**, *121*, 6569–6574.
- (40) Yan, D.-N.; Liao, C.-S.; Zhao, Y.-Q.; Liu, B.; Yang, J.-L.; Cai, M.-Q. Theoretical prediction of double perovskite $\text{Cs}_2\text{Ag}_x\text{Cu}_{1-x}\text{In}_y\text{Tb}_{1-y}\text{Cl}_6$ for infrared detection. *J. Phys. D: Appl. Phys.* **2020**, *53*, 265302.
- (41) Zhao, Y.-Q.; Ma, Q.-R.; Liu, B.; Yu, Z.-L.; Yang, J.; Cai, M.-Q. Layer-dependent transport and optoelectronic property in two-dimensional perovskite: $(\text{PEA})_2\text{PbI}_4$. *Nanoscale* **2018**, *10*, 8677–8688.
- (42) Ding, Y.-F.; Yu, Z.-L.; He, P.-B.; Wan, Q.; Liu, B.; Yang, J.-L.; Cai, M.-Q. High-performance Photodetector Based on In Se/ $\text{Cs}_2\text{XI}_2\text{Cl}_2$ (X= Pb, Sn, and Ge) Heterostructures. *Phys. Rev. Appl.* **2020**, *13*, 064053.
- (43) Pan, L.-Y.; Ding, Y.-F.; Yu, Z.-L.; Wan, Q.; Liu, B.; Cai, M.-Q. Layer-dependent optoelectronic property for all-inorganic two-dimensional mixed halide perovskite $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ with a Ruddlesden-Popper structure. *J. Power Sources* **2020**, *451*, 227732.
- (44) Ghosh, D.; Smith, A. R.; Walker, A. B.; Islam, M. S. Mixed a-cation perovskites for solar cells: atomic-scale insights into structural distortion, hydrogen bonding, and electronic properties. *Chem. Mater.* **2018**, *30*, 5194–5204.

- (45) Qian, J.; Xu, B.; Tian, W. A comprehensive theoretical study of halide perovskites ABX_3 . *Org. Electron.* **2016**, *37*, 61–73.

Graphical TOC Entry